

Local structure of Mn-doped ferromagnetic semiconductors

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Cântico Negro

*"Vem por aqui" - dizem-me alguns com os olhos doces
Estendendo-me os braços, e seguros
De que seria bom que eu os ouvisse
Quando me dizem: "vem por aqui!"
Eu olho-os com olhos lassos,
(Há, nos olhos meus, ironias e cansaços)
E cruço os braços,
E nunca vou por ali...*

*A minha glória é esta:
Criar desumanidade!
Não acompanhar ninguém.
- Que eu vivo com o mesmo sem-vontade
Com que rasguei o ventre à minha mãe*

*Não, não vou por aí! Só vou por onde
Me levam meus próprios passos...*

*Se ao que busco saber nenhum de vós responde
Por que me repetis: "vem por aqui!"?*

*Prefiro escorregar nos becos lamacentos,
Redemoinhar aos ventos,
Como farrapos, arrastar os pés sangrentos,
A ir por aí...*

*Se vim ao mundo, foi
Só para desflorar florestas virgens,
E desenhar meus próprios pés na areia inexplorada!
O mais que faço não vale nada.*

*Como, pois sereis vós
Que me dareis impulsos, ferramentas e coragem
Para eu derrubar os meus obstáculos?...
Corre, nas vossas veias, sangue velho dos avós,
E vós amais o que é fácil!
Eu amo o Longe e a Miragem,
Amo os abismos, as torrentes, os desertos...*

*Ide! Tendes estradas,
Tendes jardins, tendes canteiros,
Tendes pátria, tendes tectos,
E tendes regras, e tratados, e filósofos, e sábios...
Eu tenho a minha Loucura !
Levanto-a, como um facho, a arder na noite escura,
E sinto espuma, e sangue, e cânticos nos lábios...*

*Deus e o Diabo é que guiam, mais ninguém.
Todos tiveram pai, todos tiveram mãe;
Mas eu, que nunca princípio nem acabo,
Nasci do amor que há entre Deus e o Diabo.*

*Ah, que ninguém me dê piedosas intenções!
Ninguém me peça definições!
Ninguém me diga: "vem por aqui!"
A minha vida é um vendaval que se soltou.
É uma onda que se alevantou.
É um átomo a mais que se animou...
Não sei por onde vou,
Não sei para onde vou
- Sei que não vou por aí!*

*José Régio, in 'Poemas de Deus e do Diabo'*¹

Acknowledgments

Here is my magnum opus, the culmination of the last five years of my life. It talks about semiconductors and crystallography and lot of abstract concepts you may think is non-sense. But... why do I consider this a magnum opus?, you ask. Let me explain: doing a Doctorate, or a PhD, is a journey. And like any other journey, it has ups and downs, and a lot of turns. It is like traversing the desert, you might know where you start and maybe where you want to go, but you *will* get lost along the way, and end up in an oasis somewhere. And you are happy nonetheless.

During these years I have found happiness and heartbreak, wonder and disappointment, stress and relief, rage and unspeakable peace. It is unbelievable how much you can live in such a seemingly short amount of time. I am a most fortunate person. But what I really want to share with you, reader, is the most valuable thing I have learned: don't stop, else everything becomes gray. Color, song, breeze, aroma are as intense as you are willing to perceive them. Be curious, be willing, have an open heart, and experience as much as you can, for that is how you fulfill your soul. That is the beauty of life. And **my** life could not be more beautiful without the people that I now acknowledge.

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Preface

This thesis documents the results and analysis of experiments conducted at various institutes and large-scale facilities. The work was carried out at the Instituut voor Kern- en Stralingsfysica (IKS) of the KU Leuven (Leuven, Belgium), using the EC-SLI setup in the GHM beamline at ISOLDE-CERN (Geneva, Switzerland), and at the BM20B-Rossendorf and the BM26-DUBBLE beamlines at the European Synchrotron Research Facility (Grenoble, France). These studies were financed by the Fund for Scientific Research-Flanders, the Concerted Research Action of the KU Leuven BOF (GOA/14/007, STRT/14/002, C12/18/006 and C14/18/074), the Portuguese Foundation for Science and Technology (CERN/FIS-PAR/0005/2017), and the European Union's Horizon 2020 under grant agreements no. 654002 (ENSAR2) and no. 824096 (RADIATE). The author was awarded a Ph.D. Fellowship by the Research Foundation Flanders (FWO) for developing the work presented in this thesis.

Follow the titles and author lists of the papers on which this thesis is built:

1. Identification of the interstitial Mn site in ferromagnetic (Ga,Mn)As

T.A.L. Lima, U.Wahl, V. Augustyns, D.J. Silva, A. Costa, K. Houben, K.W. Edmonds, B.L. Gallagher, R.P. Champion, M.J. Van Bael, M.R. da Silva, J.G. Correia, J.P. Araújo, K. Temst, A. Vantomme, L.M.C. Pereira

Applied Physics Letters **106**, 012406 (2015)

2. Thermal stability of interstitial and substitutional Mn in ferromagnetic (Ga,Mn)As

T.A.L. Lima, U. Wahl, A. Costa, V. Augustyns, K.W. Edmonds, B.L. Gallagher, R.P. Campion, J.G. Correia, M.R. da Silva, K. Temst, A. Vantomme, L.M.C. Pereira

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3. Manganese segregation in (Ga,Mn)As

T.A.L. Lima, U. Wahl, V. Augustyns, K. van Stiphout, K.W. Edmonds, B.L. Gallagher, R.P. Campion, D. Banerjee, F. Kremer, K. Temst, A. Vantomme, L.M.C. Pereira

(To be submitted)

4. Manganese thermal stability in Ga-Mn-V ferromagnetic semiconductors

T.A.L. Lima, U. Wahl, A. Costa, V. Augustyns, K.W. Edmonds, B.L. Gallagher, R.P. Campion, J.G. Correia, M.R. da Silva, K. Temst, A. Vantomme, L.M.C. Pereira

(To be submitted)

Abstract

For decades, ferromagnetic semiconductors have captured the scientific community's interest, harnessing in a single material the carrier's charge as in a semiconductor and the spin as in a ferromagnet. Dilute magnetic semiconductors (DMS) are among the most well-studied families of ferromagnetic semiconductors, and pioneered multiple spintronic device concepts exploring the interactions between spin, electric current, and light. Mn-doped GaAs, the model DMS, has been regarded as the best candidate for technological application, exhibiting carrier-mediated ferromagnetism. However, despite significant progress, its ferromagnetic Curie temperature remains well below room-temperature. On the other hand, multiferroic Rashba semiconductors (MUFERS) have recently joined the class of ferromagnetic semiconductors, promising additional degrees of tunability through the precise control of spin-currents with applied electric fields, thanks to the coexistence of Rashba and Zeeman effects. In order to tune these properties in MUFERS, one must understand the interplay between the ferroelectric polarization and the magnetization, which is intrinsically related to the rhombohedral distortion of the crystal lattice. The origin of this distortion and how it influences the ferroelectricity, the ferromagnetism and their interplay are still a subject of debate. This thesis focuses on the local structure of Mn dopants in these two families of ferromagnetic semiconductors, through the investigation of their lattice location and thermal stability, providing insight on the mechanisms behind their ferromagnetic and electronic properties.

In (Ga,Mn)As, the DMS with the highest reported Curie temperature ($T_C = 185$ K), the realization of higher T_C may be enabled by a better understanding

of the out-diffusion of interstitial Mn impurities and the segregation of substitutional Mn atoms, induced by thermal annealing. In order to understand to what extent thermal annealing can be used to improve the ferromagnetic properties of (Ga,Mn)As and related compounds, we studied the lattice location and thermal stability of Mn in GaP and GaSb semiconductors, as well as in ferromagnetic (Ga,Mn)As, (Ga,Mn)Sb and quaternary (Ga,Mn)(As,X) layers, X=P or X=Sb. Across the III-Mn-V series, the tetrahedral interstitial site with anion nearest neighbors was identified as the preferred minority site occupied by Mn dopants, following the Ga-substitutional as the majority site. Moreover, the stability of interstitial Mn was found to decrease not only with increasing Mn concentration, but also with decreasing atomic packing of the host semiconductor (from GaP to GaAs to GaSb). This decrease directly affects the substitutional Mn thermal stability and results in a narrow annealing temperature range in which interstitial Mn can be removed to increase T_C . This temperature window is limited by segregation of substitutional Mn at low temperatures, which was investigated in (Ga,Mn)As films annealed at $T = 300^\circ\text{C}$, revealing the formation of disordered paramagnetic Mn-rich nanoclusters. These results further illustrate the delicate balance between structure and magnetism in III-Mn-V semiconductors, and may inspire new strategies for achieving more effective substitutional doping and higher Curie temperatures.

In (Ge,Mn)Te, the model MUFERS combining ferromagnetism with robust ferroelectric and giant Rashba effects, the ferroelectricity and its coupling to the ferromagnetism are intrinsically related to the rhombohedral distortion. Associated with this distortion is a displacement between cation and anion sub-lattices, which breaks crystal inversion symmetry. In this work the local structure of the Mn sub-lattice in (Ge,Mn)Te with Mn concentration up to 21% was investigated, and observed a smaller displacement for the Mn sub-lattice than for the host Ge sub-lattice. This is consistent with a more central, charge neutral Mn position in the lattice, which reduces the rhombohedral distortion and the ferroelectric moment at higher Mn contents in (Ge,Mn)Te. A preferential orientation of the Mn sub-lattice displacement in the ferroelectric phase was also observed, corresponding to the out-of-surface $\langle 111 \rangle$ direction, implying a possible spontaneous ferroelectric polarization. This new insight

on the nature of the sub-lattice displacement helps understanding its role in the multiferroic phase diagram, which is in turn relevant for developing future spintronic applications of (Ge,Mn)Te or materials exhibiting similar MUFERS behavior.

Beknpte samenvatting

De wetenschappelijke gemeenschap is al decennialang in de ban van ferromagnetische halfgeleiders om zowel de ladingdragers hun lading, zoals in het geval van een halfgeleider, als hun spin, zoals bij een ferromagneet, te kunnen benutten in een enkel materiaal. Verdunde magnetische halfgeleiders (DMS) behoren tot de best bestudeerde soorten ferromagnetische halfgeleiders en lagen aan de basis van verschillende concepten voor spintronics-apparaten waar de interacties tussen spin, elektrische stroom en licht verkend worden. Mn-gedoteerd GaAs, de voorbeeld DMS, wordt omwille van zijn ladingdrager-gemedieerd ferromagnetisme beschouwd als de beste kandidaat voor technologische toepassingen. Desalniettemin, ondanks significante vooruitgang, blijft zijn ferromagnetische Curie temperatuur beduidend lager dan kamertemperatuur. Anderzijds zijn de multiferroïsche Rashba halfgeleiders (MUFERS) recent toegetreden tot de klasse van ferromagnetische halfgeleiders. Dankzij het gelijktijdig aanwezig zijn van de Rashba en Zeeman effecten kunnen hun spin-stromen heel precies gecontroleerd worden door het introduceren van elektrische velden, wat leidt tot extra mogelijkheden om deze materialen af te stemmen. Om deze eigenschappen in MUFERS af te stemmen moet men de wisselwerking tussen de Ferroëlektrische en de magnetisatie begrijpen. Deze wisselwerking is intrinsiek gerelateerd aan de romboëdrische vervorming van het kristalrooster. De oorsprong van deze vervorming en hoe ze de Ferroëlektrische, het ferromagnetisme en hun wisselwerking beïnvloed is nog steeds een onderwerp van discussie. Deze thesis focust op de lokale structuur van Mn dotatieatomen in deze twee soorten ferromagnetische halfgeleiders door hun positie in het kristalrooster en thermische stabiliteit te onderzoeken en

zo inzichten te verwerven in de mechanismen achter de ferromagnetische en -elektrische eigenschappen.

Het in (Ga,Mn)As, de DMS met de hoogste gerapporteerde Curie temperatuur ($T_C = 185$ K), realiseren van een hogere T_C zou mogelijk gemaakt kunnen worden door de uit-diffusie van interstitiële Mn onzuiverheden en de segregatie van substitutionele Mn atomen, geïnduceerd door thermisch gloeien, beter te begrijpen. Om te weten in welke mate thermisch gloeien gebruikt kan worden om de ferromagnetische eigenschappen van (Ga,Mn)As en gerelateerde verbindingen te verbeteren hebben we de positie in het kristalrooster en de thermische stabiliteit van Mn in GaP en GaSb halfgeleiders, ferromagnetisch (Ga,Mn)As, (Ga,Mn)Sb en quaternaire (Ga,Mn)(As,X) lagen, met $X=P$ of $X=Sb$, bestudeerd. De tetraëdrische interstitiële positie met anionische naaste burens was de geprefereerde minderheidspositie bezet door de Mn dotatieatomen in groep III-Mn-V verbindingen, gevuld door de Ga-substitutionele meerderheidspositie. Bovendien is er gevonden dat stabiliteit van interstitiële Mn niet alleen afneemt met Mn concentratie maar ook met afnemende atomaire pakking van het gastheer materiaal (van GaP tot GaAs tot GaSb). Deze afname beïnvloedt direct de thermische stabiliteit van substitutioneel Mn en dit resulteert in een smalle regio van gloeitemperaturen waar interstitieel Mn verwijderd kan worden om zo de T_C te verhogen. Deze regio van gloeitemperaturen is bij lage temperaturen gelimiteerd door de segregatie van substitutioneel Mn, bestudeerd door (Ga,Mn)As filmen te gloeien bij $T = 300^\circ\text{C}$. Hierdoor werden ongeordende paramagnetische en Mn-rijke nanoclusters gevormd. Deze resultaten tonen aan hoe delicaat de balans is tussen de structuur en het magnetisme van III-Mn-V halfgeleiders en zouden kunnen inspireren tot het ontwikkelen van nieuwe strategieën om een hogere effectieve substitutionele dotering en dus een hogere Curie temperatuur te bereiken.

In (Ge,Mn)Te, de standaard MUFERS ferromagnetisme combineren met robuuste ferroëlektrische en giant Rashba effecten, zijn de ferroëlektrische en zijn koppeling het ferromagnetisme intrinsiek gerelateerd aan de romboëdrische vervorming. Aan deze vervorming kan een verschuiving tussen de kationische en anionische sub-kristalroosters, waardoor de inversiesymmetrie van de kristalstructuur gebroken wordt, geassocieerd worden. In deze thesis werd

de lokale structuur van het Mn sub-rooster met Mn concentraties tot 21% onderzocht en werd er een kleinere verschuiving van het Mn sub-rooster dan van het gastheer Ge sub-rooster waargenomen. Dit is in overeenstemming met een meer centrale en ladingsneutrale positie van Mn atomen in het rooster, waardoor de romboëdrische vervorming en het ferroëlektrische moment bij hogere Mn concentraties afnemen in (Ge,Mn)Te. Een preferentiële oriëntatie van de Mn sub-rooster verschuivingen was waargenomen in de richting uit het oppervlak. Dit impliceert een mogelijke spontane ferroëlektrische polarisatie. Dit nieuwe inzicht over de aard van sub-rooster verschuivingen helpt zijn rol begrijpen in het multiferroïsche fase-diagram, wat op zijn beurt relevant is in de ontwikkeling van toekomstige spintronics-applicaties met (Ge,Mn)Te of andere materialen die gelijkaardig [MUFERS](#) gedrag vertonen.

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List of Abbreviations

- DFT** density functional theory. 16, 17, 19, 20, 51, 74, 148, 150, 151
- DMS** dilute magnetic semiconductors. xv, 5, 7, 8, 11, 12, 14, 16, 27, 32, 50, 51, 64, 84, 100–102, 104, 113, 115, 119, 120, 160, 161, 171, 173, 179
- DPA** displacement per atom. 163, 164
- DW** Debye-Waller. 91
- EC** emission channeling. 37, 38, 40, 41, 153, 171
- ESRF** European Synchrotron Research Facility. 87
- EXAFS** extended x-ray absorption fine structure. 25, 37, 47, 87, 91–93, 95, 127, 148, 150, 151
- FE** ferroelectric. 25–31, 125–127, 134, 135, 143, 147, 150–152, 170, 177
- FERS** ferroelectric Rashba semiconductor. 27, 30
- FM** ferromagnetic. 11, 27–29, 31, 125–127, 148, 169, 170, 177
- FMR** ferromagnetic resonance. 29
- FMS** ferromagnetic semiconductors. 3, 5, 6, 9, 10, 30, 33, 158, 162, 163, 171
- GI-XRD** grazing-incidence x-ray diffraction. 46, 87–91
- GMR** giant magnetoresistance. 3

HR-TEM high-resolution transmission electron microscopy. 93

HR-XRD high-resolution x-ray diffraction. 87, 88, 90

IB impurity band. 13

LT-MBE low-temperature molecular beam epitaxy. 7, 14, 25, 27, 37, 52, 56, 64, 68, 84, 95, 96, 103, 104, 106, 120, 134, 142, 157, 162, 165, 172

MUFERS multiferroic Rashba semiconductor. xv, xvii, 5, 9, 24, 27, 30–32, 123, 171, 178, 179

NN nearest neighbor. 91, 92

RBS Rutherford backscattering spectrometry. 38

RKKY Ruderman-Kittel-Kasuya-Yosida quantum mechanical model for long-range magnetic interactions. 11, 12

SARPES spin and angle-resolved photoemission spectroscopy. 26

SOC spin-orbit coupling. 26

SQUID superconducting quantum interference device. 37, 47, 48, 95, 120

SR-XRD synchrotron x-ray diffraction. 87, 88, 93

TEM transmission electron microscopy. 17, 22, 51, 88, 93, 125

XAFS x-ray absorption fine structure. 17, 51, 106, 107

XAS x-ray absorption spectroscopy. 22, 46, 47

XRD x-ray diffraction. 37, 87, 125, 127, 152

Introduction

“If you had come to me a hundred years ago, do you think I should have dreamed of the telephone? Why, even now I cannot understand it! I use it every day, I transact half my correspondence by means of it, but I don’t understand it. Think of that little stretched disk of iron at the end of a wire repeating in your ear not only sounds, but words—not only words, but all the most delicate and elusive inflections and nuances of tone which separate one human voice from another! Is not that something of a miracle?”

Sir William Crookes (1903)

We are today in the *Digital Era*, experiencing the fastest shift from economies based on industrialization and goods to economies dependent on **information** and services. Information is changing the world, with *personal data* and *privacy* ever closer to becoming fundamental human rights, and with a powerful impact not only in each individual’s life, but also in society at large. I believe we are truly entering the next step within this Era, the *Information Age*.

This incredible progress stems from the deeply interwoven and near-instantaneous network that the **Internet** has become, where information spreads quicker than ever imagined. Today, we are enjoying an increasingly easy access to information, just one click away from the moment we ask *What happened yesterday in the world?*, *Where did my friends spend the weekend?*, *Which movies were selected for this year’s edition of “The Oscars”?*, *What shall I eat tonight?* But this interconnectedness stretches farther than just our daily life conundrums, it

is in the driving seat of current (social, cultural, human) events all over the world. On the one hand, a connected world brings people and their cultures closer together, all the while expanding the sphere of human knowledge. On the other hand, it also brings new challenges such as the easy spread of *fake news*, *scepticism* and *misinformation* (is the Earth flat?). Although many pages and long hours of discussion could be had about such current issues, they are beside the scope of this thesis. We are more interested the incredible **technological progress**, which was initially expressed here by Sir William Crookes, about how the telephone has transformed the world just over one hundred years ago. Would that he could see where we stand today.

Such unprecedented technological progress only became possible due to the advances in **semiconductor technology**, unceasingly increasing the amount of transistors in electronic devices, packed by billions in minuscule integrated circuits or chips. This advancement has been governed over the past decades by the famous Moore's law, "*the number of transistors in a dense integrated circuit doubles about every two years*", but is today reaching a ceiling, in which conventional electronic materials are being taken beyond their functional limits.

Contemporary electronic devices are based on silicon technology, which harnesses the *charge* of the electron, a fundamental negatively charged particle that composes most matter in the known Universe, manipulating it in various solid-state devices, e.g. computer processing units, random access memories, and, more recently, solid-state drives. In other words, we store and process **information** in our devices through an intricate control of the electron charge, in the form of electric currents or potentials. **Spintronics** introduces a new route to technological progress, overcoming the limitations of solely harnessing the electron *charge*, by introducing the additional degree of freedom of the electron *spin*. With a comprehensive control of both fundamental properties of the electron, or simply of the spin alone, *spintronics* promises a new generation of devices with numerous advantages over conventional electronics, such as non-volatility and faster operation, increased integration densities and reduced power consumption, and even new pathways to combined information processing and storage.²

In 1988, Albert Fert and Peter Grünberg discovered the giant magnetoresistance

effect (**GMR**) in spin-valve structures, which revolutionized data storage technology and awarded them the Physics Nobel prize in 2007. Integrated into our daily lives in the form of read heads of hard-disks, **GMR**-based spin-valves were then replaced by magnetic tunnel junctions, based on the tunnel magnetoresistance effect. Other examples of spintronic devices include spin-polarized light emitting diodes, spin-field effect transistors, and spin-based qubits for quantum computing.³ Whilst this first generation of spintronics, also known as *magnetoelectronics*, radicalized data storage technology, it has also created a bottleneck when combined with increasingly integrated conventional von-Neuman architectures for processing and storing information: whereas data is stored in *metal-based* magnetic devices, its processing takes place in *semiconductor-based* electronic devices. As data exchange between these two units becomes more and more time consuming and energy inefficient, a progressively attractive approach has emerged, by attempting to combine both functionalities within one sole device, the processing-in-memory approach.⁴ In other words, this has prompted a redirection of the field from *metal-based* to a *semiconductor-based* spintronics, requiring new materials where the tunability of semiconductors is combined with the characteristic spin contrast of ferromagnets.

Conventional semiconductors currently used in integrated circuits, transistors and lasers consist mainly of silicon (Si), gallium arsenide (GaAs) and gallium nitride (GaN), non-magnetic materials, while digital storage devices are typically based on ferromagnetic materials such as iron (Fe), cobalt (Co) and nickel (Ni), non-semiconducting materials. The development of spin-polarized semiconductors operating above the room temperature has been one of the most promising roads towards combining the tunability of semiconductors with the spin contrast of ferromagnets into functional spintronic materials.⁵

Ferromagnetic semiconductors (**FMS**) are a prototypical example of such materials, a pioneering development in semiconductor-based spintronics, introducing magnetic ions into non-magnetic semiconductors incurring simultaneous charge carrier spin-polarization and ferromagnetic properties. With over thirty years of an exciting history and various generations of increasing Curie temperatures and functionalities, ferromagnetic semiconductors have captured the attention of both semiconductor and magnetism communities, turning into

one of the most auspicious research topics in Material Science and Condensed Matter Physics today.

Chapter 1

Mn-doped ferromagnetic semiconductors

This chapter introduces the field of ferromagnetic semiconductors (FMS), diving into the structural, electronic and magnetic properties of both dilute magnetic semiconductors (DMS) and of multiferroic Rashba semiconductors (MUFERS), particularly Mn-doped GaAs and GeTe, respectively. First, a brief motivation and definition of the field is presented in 1.1, followed by the current understanding of (Ga,Mn)As, in section 1.2, and of (Ge,Mn)Te, in section 1.3. Detailed motivation on the local structure and its influence on material properties will follow within each chapter, culminating in the current challenges the field faces, in section 1.4.

1.1 Definition and motivation

Can we build materials that show properties of both ferromagnets and semiconductors at room temperature?

Finding the answer to this question means unwrapping one of the unsolved problems in Condensed Matter Physics today. What turned out a gargantuan quest for room-temperature ferromagnetic semiconductors (FMS) started in the decades of 1960s and 1970s, with the hype of europium chalcogenides (EuO) and chromium spinels (CdCr_2S_4 , CdCr_2Se_4),⁶ considered by some the first generation of FMS. These magnetic semiconductors are materials in which magnetism coexists with semiconducting behavior, a consequence of the inclusion of magnetic elements in their composition. This paved the way for the thorough investigation of various types of magnetic interactions, such as ferromagnetism in EuO,⁷ ferrimagnetism in EuSe,⁸ or even antiferromagnetism in EuTe.⁹ In particular, the ferromagnetic order in these materials is established by the exchange interactions between the electrons in the semiconductor bands and the localized magnetic moments from the magnetic sub-lattice. This intimate connection between two basic properties, the electrical conductivity and the magnetization, led to the discovery of new exciting effects, with implementation in the electronics industry. However, the technological realization of these ferromagnetic semiconductors was prevented by their low *Curie* transition temperatures, $T_C < 100$ K, meaning that they are far from operating at typical device temperatures, room temperature and above. Combined with both reproducibility and synthesis issues, and an crystal structure incompatible with conventional semiconductor technology, this first generation of ferromagnetic semiconductors pertained a purely academic interest, acting as vehicles towards the realization of various problems and theoretical models in magnetism in the following years.^{10,11}

In what is today a natural technological progression route, the first generation of something is followed by a second generation, and then by a third, *ad infinitum*^a. Hence, the odyssey for room-temperature ferromagnetic

^aAs an example: mobile networks (nearing 5G today) or Microsoft Windows versions.

semiconductors continued with the advent of *dilute magnetic semiconductors* in the 1980s and 1990s, brought by the widespread commercialization of non-equilibrium epitaxial growth techniques, such as low temperature molecular beam epitaxy (LT-MBE).¹² *Dilute magnetic semiconductors*, or DMS, are magnetic semiconductors in which ferromagnetism is introduced by incorporating magnetic atoms into non-magnetic semiconductors, in similarity with electrical doping, which makes insulating materials conducting by incorporating donor and acceptor dopants. In these materials the magnetic atoms are incorporated in the crystal lattice, randomly substituting a few percent of the non-magnetic atoms. A *magnetic dopant* is, in this context, an atom or an ion of an element which is different from the host constituents and that carries a non-vanishing magnetic moment - which can originate from unfilled $3d$ or $4f$ shells of transition metals or rare earths, respectively.

Two conditions carry pivotal importance in the practical implementation of DMS into spintronic devices and other applications, and are closely connected with their fundamental electronic and magnetic properties: (i) the localized magnetic moments must attain ferromagnetic order through some long-range mechanism, up to typical operation temperatures (room temperature and above); and (ii) the charge carriers in the semiconductor must be spin-polarized. Intersecting these two conditions lays the groundwork for carrier-mediated ferromagnetism in DMS, which requires an efficient coupling between spin-polarized charge carriers and the localized ferromagnetic moments, or, in other words, that charge carriers participate in the ferromagnetic ordering mechanism. Furthermore, tuning the coupling between spin-polarized charge carriers and localized magnetic moments, by controlling the splitting of the spin bands through the Zeeman interaction or magnetization and spin-currents through external electric fields, opens the door towards innovative functionalities, such as non-volatility, higher speed and lower power consumption.^{4, 13–16} These materials can be denominated as *intrinsic DMS*. This conjunction of electronic and magnetic properties automatically invalidates materials in which the ferromagnetic order and the semiconductor bands are independent of each other, or in which an efficient spin-polarization of the carriers is unlikely. Semiconductors with embedded small ferromagnetic precipitates, impurity-rich regions or even secondary-phases, are among such

materials and can be considered *non-intrinsic* or *hybrid DMS*. The distinction between *intrinsic* and *non-intrinsic DMS* is of fundamental importance and is further explored in this thesis through the investigation of the local structure of magnetic dopants in Mn-doped GaAs.

GaAs and other semiconductors combining elements from groups III and V of the periodic table (also known as III-V semiconductors, such as InAs, GaN and GaP) are well established semiconducting materials today, widely used in the electronics and optoelectronics industries with a broad range of applications. In 1992, Ohno *et al.* discovered ferromagnetism up to 35 K in Mn-doped InAs ($\text{In}_{1-x}\text{Mn}_x\text{As}$) grown by LT-MBE,¹⁷ eventually leading to the development of Mn-doped GaAs ($\text{Ga}_{1-x}\text{Mn}_x\text{As}$), with even higher transition temperatures.¹⁸ The Mn atoms introduced in these semiconductors act as acceptors, substituting for the group III elements, providing a high concentration of free holes, which in turn mediate the ferromagnetic interaction between the localized Mn moments. This carrier-mediated ferromagnetism in $\text{In}_{1-x}\text{Mn}_x\text{As}$ and $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ opened the door to new studies on spin-based phenomena in semiconductor devices, such as spin-polarized light emission,¹⁹ and electrical and optical control of the magnetization.^{20,21} Subsequently, $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ has been considered one of the best candidates for technological implementation of *DMS* materials due to the strong scientific background on GaAs, its higher Curie temperature (around 200 K)^{22–25} compared to $\text{In}_{1-x}\text{Mn}_x\text{As}$ (90 K),²⁶ and due to its diverse interesting functionalities, deriving from its carrier-mediated ferromagnetism and demonstrated in various proof-of-concept devices.²⁷

Figure 1.1 illustrates the large research volume that the *DMS* field has accrued over the past decades. Scientific interest in these compounds greatly increased just after the turn of the millennia, following the prediction of room-temperature ferromagnetism in Mn-doped GaAs and GaN by T. Dietl *et al.*²⁸ Despite major development over the last two decades, room-temperature ferromagnetism has not yet been achieved in these compounds, remaining as one of the most difficult technical challenges today.^{22,29} This problematic has steered the quest for room-temperature spintronic functionality in different directions.

The last decade has seen a building interest over the interplay between electronic structure, symmetry breaking, and spin or orbital degrees of freedom,

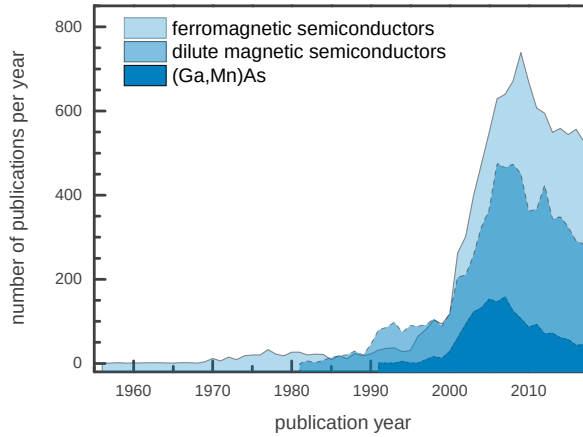


Figure 1.1: Number of publications per year, obtained from *Web of Science* using the keywords “ferromagnetic semiconductors”, “dilute magnetic semiconductors”, and “(Ga,Mn)As” in the search field *Topic*.

culminating in one of the most topical fields in condensed matter physics today, quantum materials.

Recently discovered quantum phases of matter, based on topological properties and topological phase transitions,^{30,31} are manifestations of this interplay and can be found in conventional, well-understood semiconductors. Further combining such novel properties with magnetic interactions found in ferromagnetic semiconductors, opens the door towards additional degrees of tunability, in what can be considered a *third* generation of **FMS**, multiplying their value in spintronics applications.

Multiferroic Rashba semiconductors, or **MUFERS**, are an example of such a **FMS** family which combines the breaking of inversion symmetry in a crystal through the Rashba effect, realizing a ferroelectric polarization in the crystal, with the Zeeman spin splitting induced by the magnetic exchange interaction.³² Recently, it was shown that $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$, or (Ge,Mn)Te, inherits a giant Rashba splitting of the 3-dimensional (3D) bulk states from its ferroelectric parent $\alpha\text{-GeTe}$, which can be explored in conjunction with the magnetic interaction introduced by the 3d Mn moments. (Ge,Mn)Te promises a path towards the efficient control of spin-texture via the interplay between magnetic order and electronic band structure.

This can be achieved, in particular, by aligning collinearly the ferroelectric and ferromagnetic polarization, opening a tunable Zeeman gap around the Dirac point of the Rashba bands. Moreover, this tunability has been revealed through spin-resolved photoemission experiments, in which both spin-texture and ferroelectric polarization could be manipulated through the magnetoelectric coupling by application of magnetic and electric fields.^{33,34} The control of spin helicity of the bands and its locking to ferromagnetic and ferroelectric order opens exciting new opportunities for multiferroic Rashba devices in the context of reprogrammable logic and non-volatile memory applications.

The current status of **FMS** research encompasses a series of accomplishments spread over virtually all materials families, such as derivatives of FeAs-based superconductors, e.g. $(\text{K,Ba})(\text{Zn,Mn,Fe})_2\text{As}_2$,³⁵ high Néel temperature semiconductors, e.g. LiMnAs ³⁶ and topological insulators, in which ferromagnetism might be mediated by Dirac electrons, e.g. $(\text{Bi,Mn})_2\text{Te}_3$.³⁷ Amid the vastness of the spintronics sea of opportunities, this thesis focuses on the two particular ferromagnetic semiconductor families described previously, **dilute magnetic semiconductors** and **multiferroic Rashba semiconductors**, particularly on Mn-doped GaAs and GeTe, respectively. The following sections dive deeper into their properties, exposing the interplay between local structure, thermal stability and ferromagnetism.

1.2 Manganese-doped gallium arsenide

As the most widely studied [DMS](#), Mn-doped GaAs has become the perfect demonstration of interplay between local structure and magnetic interactions, promising a vast array of applications in the field of spintronics and electronic devices.^{5,38,39} However, its *Curie* transition remains below operational temperatures, prompting a meticulous investigation into the underlying fundamental phenomena which confer it its properties. This section reviews the current understanding of the structure and magnetism of (Ga,Mn)As, focusing on aspects of interest to further increase T_C .

1.2.1 Ferromagnetic interactions

Ferromagnetism in Mn-doped GaAs stems from the interaction between spin-polarized charge carriers and the localized Mn^{2+} magnetic moments. There are two theoretical models describing the charge-carrier mediated ferromagnetism in (Ga,Mn)As: (i) the mean-field *p-d* Zener model, and (ii) the impurity band model. While heatedly debated for over a decade, it is accepted today that it is the first model which describes the [FM](#) interactions in highly-doped metallic (Ga,Mn)As layers, for Mn concentrations larger than $x_{\text{Mn}} > 0.02$.^{b40}

The *p-d* Zener model (i) was first proposed in 1951 by Clarence Zener as a model for the role of band carriers in promoting ferromagnetic ordering between localized spins in magnetic metals.⁴¹ Accordingly, through a *p-d* exchange coupling with localized magnetic moments, charge carriers become spin-polarized, redistributing them through the spin-split sub-bands and lowering their energy, thus allowing for ferromagnetic ordering to emerge. In accordance to the Ruderman-Kittel-Kasuya-Yosida ([RKKY](#)) quantum mechanical treatment, the sign of the resulting interaction between localized spins oscillates with the spin-spin distance, indicating that the [RKKY](#) and Zener models are equivalent within the continuous and mean-field approximation.⁴² This approximation is

^bIn this case, x_{Mn} is defined as x in $\text{Ga}_{1-x}\text{Mn}_x\text{As}$, i.e. of substitutional Mn, in the absence of interstitial Mn. However, throughout this thesis, unless otherwise specified, x and x_{Mn} are defined as the concentration of Mn atoms divided by the sum of the concentrations of Mn and of cation (Ga) atoms, i.e. including substitutional and interstitial Mn.

valid as long as the period of [RKKY](#) oscillations is large compared to the average distance between localized spins. Ergo, the mean-field Zener model is sufficient to describe ferromagnetic interactions in [DMS](#), as the distance between charge carriers in these materials is typically of the same magnitude as the distance between spins, i.e. the carrier concentration is of the same order as the dopant concentration $p \lesssim x$, where p is the carrier density, x the dopant atom density.

Microscopic models of the electronic structure of metallic (Ga,Mn)As assert that Mn acceptors occupy substitutional lattice sites, Mn_s , stabilizing in a $3d^5 + h^+$ configuration, i.e. with Mn^{2+} charge state and producing a bound hole.^{43,44} According to Hund's rules, the five occupied $3d$ orbitals in Mn_s^{2+} form a localized $S = 5/2$ magnetic moment, which interacts with delocalized charge carriers through $p-d$ Zener exchange, hybridizing d orbitals and valence band p orbitals. Consequently, the hole states in the valence band, which can be described using the Kohn-Luttinger parameterization for GaAs,⁴⁵ become spin-polarized. This exchange interaction can then be characterized by a single constant, J_{pd} .

Holes in (Ga,Mn)As are considerably more efficient in mediating spin-dependent interactions between localized spins, due to a higher density of states and to larger exchange coupling to Mn spins. In other words, by coupling with a localized Mn $3d^5$ moment, a $2p$ valence band electron-hole will become spin-polarized, and since holes are weakly localized in the (Ga,Mn)As lattice they'll interact with other Mn moments, leading to ferromagnetic ordering.²⁸ This approach has successfully described a number of properties observed in ferromagnetic [DMS](#), in particular in (Ga,Mn)As, such as the ferromagnetic transition temperature T_C , magnetization, electron-hole liquid spin-polarization, and strain- and temperature-dependent magneto-crystalline anisotropy (cf. reviews [5, 27, 39, 46]). Furthermore, this model predicts a monotonic increase in T_C with effective Mn concentration x_{eff} and with carrier density, with no fundamental limit to T_C below room temperature.⁴⁷ Effective Mn concentration x_{eff} accounts for the inclusion of compensating defects, further described in the next section [1.2.2](#).

In contrast, the impurity band model (ii) proposes that ferromagnetism in [DMS](#) is mediated by localized dopant-derived states, between $3d$ holes through

superexchange.^{48,49} Within the relevant hole concentration range, the Mn_s^{2+} impurity band (IB) and valence bands do not merge, and the Fermi level is located within IB. In this scenario, T_C will depend on the localization of $3d^5 + h^+$ states: states in the center of the IB are extended and maximize T_C , while states towards the top or bottom of the IB are more localized, reducing T_C . In other words, the $3d$ holes that lie in the IB hop between the localized Mn atoms, mediating the ferromagnetic ordering. In this model, the Curie temperature is independent of effective Mn concentration and is not hindered by the presence of compensating effects, which can be essential for the localization of the Fermi level inside the impurity band.

The complex long-range ferromagnetic exchange mechanism at play in Mn-doped GaAs delivered a true *Battle of the Bands*, as named by Nitin Samarth in Ref. 50, where two schools of thought aimed at establishing either model as the correct one. On the one hand, Dobrowolska *et al.* reported a non-monotonic variation of T_C up to a rather high nominal concentration of Mn in (Ga,Mn)As, by combining ion channeling measurements for Mn lattice location with magnetization, transport and magneto-optical data.⁵¹ Additionally, Cho *et al.* have also observed a natural limit for T_C in (Ga,Mn)As, as charge-carrier concentration equals x_{eff} ,⁵² threshold above which T_C goes to zero and ferromagnetic order disappears altogether. Both of these studies are consistent with the IB exchange model, but have only focused on the insulator side of the metal-to-insulator transition of (Ga,Mn)As. Wang *et al.* disputed these results by demonstrating that the carrier density in annealed metallic (Ga,Mn)As films can be directly compared to the effective Mn concentration x_{eff} .²⁵ In other words, in weakly compensated metallic systems, T_C and electrical conductivity do not go to zero as charge-carrier concentration equals effective Mn content, pertaining its ferromagnetic interactions. This was further emphasized by Zhou *et al.* in Ref. 40, where they observed a monotonic increase in T_C with charge carrier density in (Ga,Mn)As and related compounds, by shifting of the Fermi level by means of carrier compensation through helium-ion irradiation. Both these reports are consistent with the previously well established *p-d* Zener model. Ultimately, both mechanisms are likely valid, depending on the concentration of substitutional and interstitial Mn as well as of other defects: the IB-model is

more valid at lower Mn concentrations, on the insulator side of the metal-to-insulator transition, while the p - d Zener model better reproduces the metallic high-concentration regime. In particular, a transition between the types of mechanisms has been observed by Cubukcu *et al.*,⁵³ where (Ga,Mn)(As,P) layers doped with 10% Mn steadily change from a metallic to an insulator state as P concentration is increased.

1.2.2 Compensation by interstitial impurities

As described previously, in typical high T_C (Ga,Mn)As thin films with several % Mn content, Mn atoms are incorporated in Ga-substitutional sites, providing both the localized magnetic moments and the itinerant holes which mediate the magnetic coupling. Hence, a large charge carrier concentration is essential for achieving the highest possible Curie temperatures in these systems. However, due to the low growth temperature, 200°C-260°C, and low solubility of Mn in GaAs, two types of hole compensating crystalline defects can be unintentionally formed during synthesis: the arsenic antisite (As_{Ga}), and the manganese interstitial (Mn_i).⁵⁴ The first, the arsenic antisite As_{Ga} , is a common defect formed during LT-MBE growth of GaAs,^{55,56} where As atoms occupy Ga-substitutional sites and act as double donors, compensating the natural p -type nature of (Ga,Mn)As films. As_{Ga} antisites are stable up to temperatures of about 450°C,⁵⁷ well above the transition temperature from a uniform DMS to a multiphase structure with metallic MnAs precipitates, and can reach densities of 10^{20} cm^{-3} , accounting for up to 1% of Ga sites, the same order of magnitude as typical Mn doping levels.⁵⁸ The incorporation of these compensating defects can, however, be minimized during LT-MBE growth, by a precise control of temperature and As-Ga stoichiometry in deposited epilayers.^{56,59}

The second compensating defect present in high-quality, high- T_C (Ga,Mn)As layers is the Mn interstitial Mn_i . During growth a majority of Mn atoms is incorporated as Ga-substitutionals, Mn_s , while a minority fraction occupies interstitial sites (Mn_i), with a significant concentration in as-grown structures as Mn content is increased.^{29,60} The Mn interstitial defects have a two-fold compensating effect: (i) magnetic, as there is an antiferromagnetic coupling

between Mn_i and Mn_s pairs through a superexchange interaction, and (ii) electric, since double donor Mn_i compensates Mn_s acceptors.^{29,60–62} On the other hand, the Mn interstitial has a higher mobility than As-antisites and can be partially removed by low temperature annealing.^{48,60}

As will be discussed in more detail throughout this thesis, the magneto-electronic behavior of (Ga,Mn)As is significantly affected by the concentration and thermal stability of Mn atoms. For a given Mn_s concentration, Mn_i self-compensation modulates the hole concentration, the Fermi level, and the effective x_{eff} concentration of non-compensated Mn_s moments. Furthermore, this balance between Mn_i and Mn_s concentrations is an essential player in the two figures of merit of (Ga,Mn)As films, Curie temperature (T_C), and effective magnetization,²⁹ and can be directly linked to the debate on the basic mechanisms of magnetic interaction in Mn-doped III-V DMS, *p-d* Zener model versus impurity-band *d-d* superexchange model.^{25,40,50,51}

As seen in the previous section, T_C increases with effective Mn concentration, which takes into account the balance between the fractions of Mn substituting for Ga (Mn_s) and of Mn in interstitial sites (Mn_i). Since Mn_i is both a double donor and couples with Mn_s through an antiferromagnetic interaction, the effective Mn concentration x_{eff} , that contributes to the observable ferromagnetism in (Ga,Mn)As, is smaller than the nominal concentration x_{Mn} by twice the Mn_i concentration x_i , $x_{\text{eff}} = x_{Mn} - 2x_i$. Consequently, the hole concentration p will be smaller or at least of the order of $p \lesssim (x_{Mn} - 2x_i)N$, where N is the density of Ga atoms in the crystal. Although the incorporated Mn content in high-quality (Ga,Mn)As has increased throughout the years beyond the solubility limit, up to $x_{Mn} = 20\%$, the Curie temperature T_C has been observed to saturate close to 200 K for concentrations $x_{Mn} > 10\%$.^{63,64} Moreover, the highest T_C and p values achieved in (Ga,Mn)As have been obtained after thermal treatment close to growth temperature, at annealing temperatures between 160°C and 210°C.²² Transport measurements have demonstrated a partial activation by annealing that results from the out-diffusion of a compensating defect with a low thermal stability, with an activation energy of $E_a = 0.7$ eV.⁶⁰ This report was supported by *ab initio* calculations yielding similar activation energies for Mn_i diffusion bound in different local structure configurations,^{29,60,65} proposing

that Mn_i diffuses towards the interfaces, surface and substrate, where it becomes passivated, partaking in the formation of antiferromagnetic MnO surface films,^{24,60,66} or MnAs monolayers.⁶⁷

A possible solution for investigating the T_C and effective magnetization limitations comes from engineering the composition of Mn-doped GaAs, through the introduction of other group V elements in arsenic sites. This has been studied over the past decade in quaternary $(\text{Ga,Mn})(\text{As,X})$ layers, $\text{X}=(\text{P,Sb})$, where the introduction of group V elements resulted in further degrees of freedom in which to tune magnetic and electric properties, particularly magnetic anisotropy, band gap, and carrier concentration.^{68–71} As an example, the addition of P to $(\text{Ga,Mn})\text{As}$ layers allows for a precise control and switching of the magnetic anisotropy through epitaxial strain,^{68,72,73} and even the tuning of magnetic domain-wall motion associated with carrier spin drift velocities in $(\text{Ga,Mn})(\text{As,P})$.^{74–76} On the other hand, DFT studies predicted a linear decrease in T_C with increasing P doping,⁷⁷ and no further improvement has been observed up to date. In contrast, doping with Sb has been predicted to decrease the tendency for self-compensation, due to the weaker bonding between host atoms, but with the caveat of a degraded crystal quality, ultimately decreasing effective Mn concentration.^{71,78,79} This has also opened the path towards tuning of the anisotropic magnetoresistance as a function of alloy composition.^{70,71}

$(\text{Ga,Mn})\text{Sb}$ is another Mn-doped III-V DMS with similar properties to $(\text{Ga,Mn})\text{As}$, which is expected to contain lower magnetic compensation due to a larger lattice constant and weaker bonding between host atoms.^{80,81} However, a detailed understanding of the $(\text{Ga,Mn})\text{Sb}$ phase diagram is still lacking, as its synthesis into a dilute magnetic matrix remains challenging.^{82,83} Both MnSb and MnAs ferromagnetic inclusions have been observed in $(\text{Ga,Mn})\text{Sb}$ layers, with large blocking temperatures and providing high superparamagnetic T_C , limiting substitutional Mn incorporation and ferromagnetic T_C .^{84–89}

Despite its central role in the understanding of both magnetic and electronic properties in $(\text{Ga,Mn})\text{As}$ and other Mn-doped III-V DMS, interstitial Mn is far from being a well understood defect. The following sections take a deeper look at how the local structure of both substitutional and interstitial Mn in $(\text{Ga,Mn})\text{As}$ and the III-Mn-V DMS family influences their structural and magneto-electronic

properties, aimed at achieving higher- T_C spintronic materials.

1.2.3 Manganese lattice location in gallium arsenide

Mn-doped III-V semiconductors such as (Ga,Mn)As in particular, display crystallographic structures of the $F\bar{4}3m$ group, a cubic *zincblende* crystalline group. There are several possible interstitial sites in the structure of Mn-doped GaAs – tetrahedral (T), bond centered (BC), anti-bonding (AB) among others, as illustrated in Fig. 1.2. To identify which site can be occupied by dopants such as Mn, various experimental techniques can be employed, either based on channeling of charged particles (ions or electrons), or on probing the atomic environment of the dopant atom, e.g. in x-ray absorption fine structure (XAFS) techniques.

Early reports on the lattice location of Mn dopants in GaAs report both a pure Ga-substitutional incorporation (using XAFS),⁹¹ and a mixed Ga-substitutional and T interstitial occupancy (by ion channeling⁹² and XAFS)⁹³ with the majority of the atoms in substitutional sites. Although consistent with Mn_i occupying tetrahedral (T) interstitial sites, the measurements did not allow to discriminate between the two nonequivalent T sites in zincblende GaAs: coordinated by four Ga atoms (T_{Ga}) or by four As atoms (T_{As}).^{90,94} More recently, XAFS experiments confirmed the mixed occupancy and identified T_{Ga} as the most likely interstitial site for Mn atoms in GaAs.^{95,96} However, XAFS is not well suited to distinguish elements with similar atomic numbers, as is the case for Ga and As, especially in cases of multi-site occupancy (substitutional and interstitial) where the site to be identified is in fact the minority one (interstitial). On the other hand, density functional theory (DFT) calculations yielded lower formation energy for Mn in T_{As} sites compared to T_{Ga},⁶⁰ consistent with Mn cations coordinated by As anions as nearest neighbors. Additionally, T_{As} has been predominantly observed in transmission electron microscopy (TEM) measurements using (002) diffracted beam.⁵⁵ Pioneering work using x-ray scattering techniques probed Mn lattice location in GaAs, and reported comparable T_{Ga} and T_{As} occupancies.^{97–99} Coexisting T_{Ga} and T_{As} occupancies would suggest that the Mn_i lattice site depends on the presence of neighboring

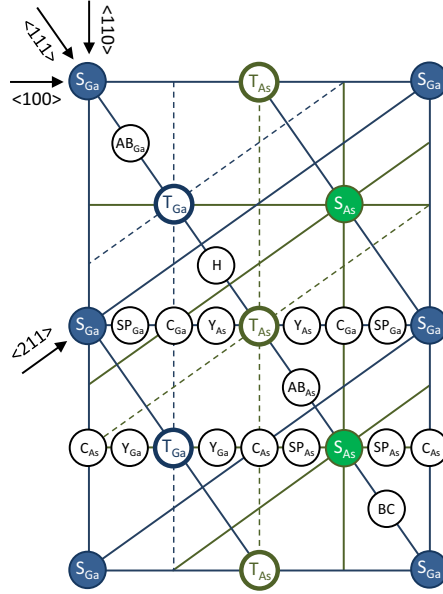


Figure 1.2: Figure extracted from Ref.⁹⁰ The $\{110\}$ plane in GaAs zincblende lattice, showing the following sites: the substitutional Ga (S_{Ga}) and As (S_{As}) sites; the tetrahedral interstitial sites with Ga (T_{Ga}) and As (T_{As}) nearest neighbors; interstitial sites along the $\langle 111 \rangle$ direction, i.e. the bond center (BC), antibonding Ga (AB_{Ga}), antibonding As (AB_{As}), and the hexagonal site (H); and the interstitial sites along the $\langle 100 \rangle$ direction, in either Ga or As rows, i.e. the split interstitials (SP_{Ga} and SP_{As}), the "C" sites with C_{2v} symmetry (C_{Ga} and C_{As}), and the "Y" sites (Y_{Ga} and Y_{As}). Along the $\langle 100 \rangle$, $\langle 111 \rangle$, $\langle 110 \rangle$ and $\langle 211 \rangle$ directions, the rows of Ga and As atoms are indicated (lines), as the rows of the T_{Ga} and T_{As} sites (dashed lines). Note that, along the $\langle 111 \rangle$ direction, the substitutional (S_{Ga} and S_{As}) and tetrahedral interstitial (T_{Ga} and T_{As}) sites are all located on the same row; along the $\langle 100 \rangle$ direction, S_{Ga} is on the same row as T_{As} , and S_{As} is on the same row as T_{Ga} .

Mn_s atoms, i.e. that isolated Mn_i and interstitials in Mn_i - Mn_s pairs should occupy different T sites. This is however in contradiction with DFT calculations which predicted that, for typical ferromagnetic (Ga,Mn)As samples, where the Mn_s concentration is the large majority over that of Mn_i , T_{As} is the most stable site, regardless of Mn_i being isolated, in Mn_i - Mn_s pairs, or even in Mn_s - Mn_i - Mn_s triplets.⁶⁵

Solving this inconsistency would allow for a better understanding of the mechanisms of electric and magnetic compensation by Mn_i which, as introduced above, plays a central role in the behavior of (Ga,Mn)As. Establishing the lattice location of Mn in (Ga,Mn)As requires the use of a technique which can unambiguously distinguish between the two T sites. Emission channeling is a technique uniquely suited to address this problem, and was used in a recent study on GaAs in the very low concentration regime, $x < 0.05$ at. %, with different electronic doping (undoped, *p*-type and *n*-type)^{90,94} to identify the lattice location and thermal stability of Mn atoms. In these reports, the Mn atoms were found to occupy mainly the substitutional site with a minor fraction on the T_{As} interstitial site. This interstitial was observed to diffuse at temperatures around 400°C, converting from interstitial to substitutional sites. This diffusion temperature is, however, higher than reported in literature for (Ga,Mn)As in the high Mn concentration regime.^{29,60} Additionally, these experiments were performed on GaAs within the very low Mn doping regime ($x < 0.05$ at. %), which might point towards a concentration dependent mechanism modifying the local structure and magneto-electronic properties of the material at higher concentrations.

1.2.4 Manganese thermal stability

In order to further increase T_C in (Ga,Mn)As and related compounds, most studies focused on a careful optimization of the synthesis and post-growth treatments in (Ga,Mn)As layers with a high Mn concentration (several percent). Interstitial Mn out-diffusion has been observed during thermal annealing treatments in the temperature range 160°C–200°C.^{22,25,60,100} Understanding the diffusion mechanism of interstitial Mn becomes then crucial, as it presents

itself as a limiting factor in the optimization of T_C through thermal annealing in (Ga,Mn)As. At higher Mn concentrations, mechanisms such as the binding energy of the interstitial Mn to substitutional atoms have been suggested to increase interstitial stability, which would directly hinder its diffusion and, consequently, removal from the (Ga,Mn)As layer.^{65,101,102} Moreover, increasing Mn content increases the fraction of Mn in higher complexity structures, such as Mn_s - Mn_i pairs, further enhancing the thermal stability of interstitial Mn.

On the other hand, the diffusion and segregation of *substitutional* Mn also plays a central role on the magnetic and structural properties of (Ga,Mn)As. Experiments based on ion channeling showed that part of the substitutional Mn is converted to a non-substitutional (random) component at temperatures as low as $\sim 280^\circ\text{C}$.⁹² Additionally, a detailed study of the dependence of T_C on annealing temperature revealed a decrease in T_C with increasing annealing temperature in the range 160 - 220°C .²² These temperatures are, however, well below the well-understood regime of secondary phase formation ($> 400^\circ\text{C}$), described in the next section (cf. 1.2.5), and direct evidence for Mn_s segregation below this temperature is lacking. Consequently, the thermal stability of both interstitial Mn and the segregation of substitutional Mn in (Ga,Mn)As remain poorly understood property at several percent Mn doping.

Doping (Ga,Mn)As layers with other group-V elements, such as P or Sb, has in some cases been predicted to reduce Mn_i self-compensation.^{71,79} Extensive studies have been performed on the incorporation of phosphorus (P) dopants in (Ga,Mn)As layers, which introduce a tunable strain which allows for a precise control and switching of the magnetic anisotropy.^{73,103} *Ab initio* theoretical studies in these compounds, (Ga,Mn)(As,P)⁷⁹ predict that P doping adds a weaker tendency for self-compensation to the layers due to an increase in interstitial Mn formation energy, decreasing its concentration at P contents ~ 0.25 . Contrarily, DFT studies in Ref. 77 anticipated a linear decrease in T_C with increasing P doping, which was then further emphasized by micromagnetic studies on (Ga,Mn)(As,P) layers in Ref. 72. These measurements show that the P concentration actively influences the magnetic anisotropy parameters, resulting in a reduced hole density, conductivity, and Curie temperature.⁷² On the other hand, for sufficiently large P content, epitaxial strain can be

engineered such that the magnetic anisotropy can be switched from an in-plane magnetic axis to an out-of-plane,⁶⁸ with significant increase in coercive field.¹⁰⁴

Also the incorporation of Sb in (Ga,Mn)As layers has been investigated, where an accurate control of anisotropic magnetoresistance is possible by tuning of the alloy composition.⁷⁰ Increasing Sb content in (Ga,Mn)(As,Sb) layers causes an increase in the lattice constant, according to Vegard's law, which was predicted to increase T_C for low Sb contents, while decreasing effective Mn concentration for higher contents.⁷¹ In the work described in Ref. 71, T_C remains proportional to x_{eff} and $p^{1/3}$ at low Sb contents, which is consistent with the Zener model. However, T_C is still smaller than analogous conventional (Ga,Mn)As films, and is attributed to the introduction of disorder and defects by the incorporation of a heavy element.⁷¹ (Ga,Mn)Sb displays the opposite end of this effect, in which the weaker bonding between Ga and Sb atoms results in lower magnetic compensation, but also charge carrier concentration and, consequently, T_C .^{80,81} Additionally, this weaker bond decreases the stability of Mn dopants, resulting in the observation of both MnSb and MnAs ferromagnetic inclusions in (Ga,Mn)Sb layers, with large blocking temperatures, high superparamagnetic T_C , and a very low diluted ferromagnetic T_C .^{84–89} Albeit a detailed understanding of the (Ga,Mn)Sb phase diagram is still lacking, due to a challenging synthesis into a dilute magnetic matrix,^{82,83} its lower self-compensation agrees with either a decreased thermal stability of interstitial Mn impurities or a higher formation energy than in (Ga,Mn)As.

Further investigating the structure and magnetism of quaternary (Ga,Mn)(As,X) compounds may provide a more comprehensive understanding of the mechanisms behind Mn incorporation and diffusion in (Ga,Mn)As. As bonding strength between Ga and X decreases from phosphorus to arsenic to antimony, the self-compensation brought by interstitial Mn appears to also decrease at the same time as it compromises the structural stability of the layer, possibly due to a lower Mn_s thermal stability.

Unraveling the thermal stability of both substitutional and interstitial Mn dopants in these III-Mn-V compounds becomes then essential in the understanding of the mechanisms hindering the optimization of T_C and effective magnetization.

1.2.5 Formation of secondary phases

The thermal treatment of Mn-doped GaAs layers has been not only the preferred method to achieve high- T_C in *diluted* systems, but also widely employed in the fabrication of *hybrid* ones, in which ferromagnetic MnAs nanoclusters are embedded in a paramagnetic GaAs:Mn matrix.^{105–108} The formation of a hybrid phase with embedded MnAs nanoclusters is also seen as a promising alternative in the field of spintronics, as the nanoclusters can show ferromagnetic behavior even at room temperature.^{13,39,109} Stacking these hybrid structures into heterostructures with semiconductors and/or metallic layers raises interesting effects such as a large tunneling magnetoresistance ratio observable at room temperature,^{110,111} or giant magnetoresistance effects in layered structures.^{112,113} These effects are modulated by the structural and magnetic properties of the MnAs nanoclusters embedded in the GaAs:Mn layer, and can be tuned by adjusting, e.g. cluster size, shape and/or distribution in the host material.¹⁰⁸

Naturally, above its solubility limit in GaAs, Mn segregation into nanoclusters is already possible during sample growth.^{114,115} However, a diverse and precise tuning of their properties can be achieved through thermal annealing, typically for temperatures above 400°C and at various Mn contents.^{108,112,113} Over the past decades, two types of clusters have been extensively characterized: small *zincblende* MnAs nanoclusters, and larger *NiAs-type* MnAs nanoclusters.^{101,102,116,117} In most studies, variations of both types of nanoclusters have been found together within hybrid GaAs:MnAs layers, annealed at temperatures ranging from 500°C to 700°C, and Mn concentrations from very low, 0.1%, to close to the solubility limit, 20%. However, a few trends have been identified: annealing (Ga,Mn)As layers at relatively low temperatures ($\sim 500^\circ\text{C}$) leads to Mn segregation into small *zincblende* nanoclusters, while at higher temperatures ($\sim 600^\circ\text{C}$) already results in the formation of larger, hexagonal *NiAs-type* nanoclusters.^{101,102,107,116–123} Transmission electron microscopy (TEM)¹⁰¹ and x-ray absorption spectroscopy (XAS)¹²⁴ experiments have shown that *zincblende* MnAs nanoparticles grow coherently with the surrounding GaAs host lattice with diameters between

2 nm and 10 nm. On the other hand, *NiAs-type* MnAs nanoclusters solidify in larger sizes, 20-50 nm, and are strained within the GaAs:Mn structure.¹²⁵ Their deformation has also been observed to introduce strain in the GaAs:MnAs layers, dependent on the processing conditions and primary structure defects, and independent from Mn concentration.¹²⁶

Both types of MnAs nanoclusters display ferromagnetic properties above room temperature dependent on Mn content: at low concentrations, below 1% Mn, hybrid GaAs:MnAs layers combine both ferromagnetic and superparamagnetic behavior; above 1% Mn, only superparamagnetic behavior has been observed.¹¹⁷ The characteristic T_C of both types also differs, with $T_C \sim 350$ K for *zincblende* MnAs nanoclusters, and a variable T_C between 330 K and 370 K for *NiAs-type*.^{116, 119, 127} Additionally, the T_C of both types of nanoclusters is higher than for bulk MnAs in hexagonal *NiAs* structure, with a T_C of 318 K.¹²⁸

Most research to date has focused on these clear tendencies, yet it remains challenging to predict which kind of nanoclusters is formed based solely on the annealing conditions and Mn content of the layer. Little attention has also been devoted to annealing at lower temperatures, between 200°C and 400°C, where the ferromagnetism in (Ga,Mn)As layers is greatly reduced, albeit no well-defined secondary phases have been observed. Furthermore, ion-channeling experiments observed indications of an early segregation onset at these temperatures, as low as 282°C,⁹² effectively decreasing T_C in the (Ga,Mn)As layer.

1.3 Manganese-doped germanium telluride

Manganese-doped germanium telluride, (Ge,Mn)Te, has in recent years become the model multiferroic Rashba semiconductor, **MUFERS**, by combining its ferromagnetic properties with a robust ferroelectricity and a giant Rashba splitting.^{33,34,129,130} This section reviews the current understanding of the structural and multiferroic properties of (Ge,Mn)Te. First, section 1.3.1 focuses on the ferroelectric distortion inherited from GeTe, and second, section 1.3.2 explores the interplay between ferromagnetism and ferroelectricity in (Ge,Mn)Te from a local structure perspective.

1.3.1 Ferroelectric distortion

Mn-doped GeTe inherits its ferroelectric properties from GeTe, a narrow-gap semiconductor, and one of the simplest ferroelectrics with only two atoms per primitive unit cell.^{131,132} Ferroelectricity in GeTe is derived from the peculiar *resonant bonding* between Ge cations and Te anions, which stems from the superposition of equivalent virtual states that form saturated bonds with only half of the neighbors.^{133,134} This bonding forces a lattice stabilization in a distorted configuration, with alternated short strong bonds and long weaker ones,^{135,136} and leads to three relevant effects: (i) a highly delocalized and polarizable *p* electron density, (ii) an unconventional *resonant bonding* epitaxy, and (iii) a distortion of the rocksalt unit cell to rhombohedral. The first (i) plays a substantial role in (Ge,Mn)Te, where the polarized charge carriers mediate ferromagnetism through an RKKY interaction.³² In the second effect (ii), *resonant bonding* directly influences epitaxial crystallization of GeTe layers, reducing the contribution from interface energy and potentially diminishing defects in the film.¹³⁷ Lastly, this unconventional bonding results in a Jahn-Teller distortion (iii), which distorts the rocksalt unit cell along the $\langle 111 \rangle$ direction, transforming it into a rhombohedral structure, coined as the α -phase of GeTe.¹³⁸ This ordered rhombohedral distortion forces a shift of the Ge sub-lattice with respect to the Te atoms, where both sub-lattices no longer share the same center of charge, and a ferroelectric polarization is induced.^{139–141}

α -GeTe undergoes a spontaneous paraelectric to ferroelectric phase transition at a critical temperature $T_C^{FE} \sim 700$ K,^{131,142} below which the $Fm\bar{3}m$ symmetry of the cubic rocksalt structure is broken, forming a polar rhombohedral $R\bar{3}m$ α -phase by elongation of the unit cell along the $\langle 111 \rangle$ direction. The rhombohedral distortion in GeTe is non-centrosymmetric due to a large relative displacement between Ge and Te sub-lattices, of as much as 0.31 Å,^{142,143} establishing the ferroelectric (FE) polarization along the $\langle 111 \rangle$ direction. Moreover, the ferroelectric dipolar moment exists spontaneously at a longer range, without previous polarization by an external field, i.e. below T_C^{FE} there is a net FE polarization in the material. This is a consequence of the favorable ordering of the distorted bonds which acts like a driving force, guiding and aligning the polarization direction in neighboring crystalline unit cells.

Ferroelectric α -GeTe is a naturally p -type semiconductor with an indirect band gap of 0.5 eV, the Fermi level inside the valence band,¹⁴⁴ and carrier concentrations of the order of 10^{20} cm⁻³.^{34,145,146} This unusually large hole concentration stems from a non-negligible concentration of Ge vacancies, in the order of 8-10% in GeTe crystals, as experimentally claimed by EXAFS studies in Ref. 147. Each vacancy acts as an acceptor and contributes with two holes to the charge carrier density, playing an essential role in the conductivity of GeTe. Moreover, Edwards *et al.*¹³⁴ predicted that Ge vacancies have a low formation energy, possibly forming spontaneously during LT-MBE growth as an intrinsic property of the material. Fukushima *et al.*¹⁴⁸ further extended this prediction by estimating comparable formation energies between Ge-vacancies and Mn_{Ge} substitutionals, anticipating that this large Ge-vacancy concentration would carry over to Mn-doped GeTe, providing the spin-polarized charge carriers that mediate the $p-d$ ferromagnetic interaction.^{32,129} Additionally, Ge-vacancies can play a significant role in other aspects of GeTe, such as the phase switching mechanism,¹⁴⁹ thermal and thermoelectric properties,¹⁵⁰ or even granting topological insulator properties to Ge(Sb,Te) compounds.¹⁵¹ An overview of these effects is outside the scope of this thesis and the reader is referred to cited literature.

In both undoped and Mn-doped GeTe, the displacement between cation (Ge or Mn) and anion (Te) sub-lattices, induced by the FE distortion, breaks crystal

space inversion symmetry, lifting the degeneracy of (surface) electronic spin bands through the spin-orbit interaction, or spin-orbit coupling (SOC).^{152–154} This is a well-known phenomenon in classical semiconductors, the *Rashba* effect, which occurs for example at a (semiconductor) interface or surface, and results from the interaction between charge carriers and an electric field perpendicular to the interface. In α -GeTe crystals, charge carriers travelling parallel to the interface experience the perpendicular electric field, generated by the spontaneous ferroelectric moment, as an effective magnetic field, which lifts the spin degeneracy and splits the electronic bands into two bands with opposite spins.^{130, 155} This Rashba-splitting of the electronic bands, with corresponding helical spin texture, can be described by:

$$E_{\pm}(k) = \frac{\hbar^2 k^2}{2m^*} \pm \alpha_R k \quad (1.1)$$

where $\hbar$ is the reduced Planck constant, k is the momentum, m^* is the effective electron mass, and α_R is the *Rashba parameter*, a constant representing the strength of the Rashba effect. α_R is proportional to the electric field induced by the inversion symmetry breaking and to the strength of the SOC, which depends on the atomic mass. The larger the symmetry breaking, the larger the Rashba spin splitting becomes.^{156–159} The Rashba parameter is typically rather small in conventional semiconductor interfaces, with $\alpha_R = 0.07$ eV Å for InGaAs/InAlAs as an example, but reaching a Rashba-splitting as high as $\alpha_R = 3.8$ eV Å in more recently discovered polar bismuth tellurohallide compounds BiTeX (X=I, Br, or Cl).^{158, 160} Even with a very large spin-splitting, however, these materials lack the possibility to switch or tune the spin texture by external means, an important feature for functionalization. This limitation can be overcome in GeTe and related compounds, where the Rashba spin splitting is strongly influenced by the local FE polarization, resulting in a giant bulk Rashba splitting with $\alpha_R = 4.8$ eV Å, the highest recorded for any material up to date and in good agreement with predictions.^{161–163} This giant Rashba-splitting has been demonstrated for α -GeTe using spin and angle-resolved photoemission spectroscopy (SARPES) experiments,¹⁶¹ revealing not only the large lateral band splitting but the counter-helical spin texture of the Rashba bands as well. Furthermore, the direction of the effective Rashba magnetic field can then

be switched by simply reversing the FE polarization, and controlled through an external electric field, a promising feature for spin texture manipulation in spintronics applications.^{139,140} The presence of a giant Rashba effect in ferroelectric GeTe has coined it the term *ferroelectric Rashba semiconductor* or *FERS*.¹⁵⁵

1.3.2 Local structure, magnetism and electronic structure

Manganese-doped GeTe, or (Ge,Mn)Te, is a *multiferroic Rashba semiconductor* (*MUFERS*) where ferroelectricity and ferromagnetism coexist and interact. Doping GeTe crystals with Mn induces ferromagnetism in a similar fashion to the prototype *DMS* (Ga,Mn)As.^{164,165} The ferromagnetic interaction has been shown to be mediated by the high density of spin-polarized holes, provided by Ge vacancies, following an RKKY exchange mechanism.^{166,167} Contrary to (Ga,Mn)As, Mn^{2+} dopants in (Ge,Mn)Te do not act as acceptors, i.e. do not contribute to hole concentration, allowing for an independent study of magnetization of Mn and hole density.¹⁶⁸ FM Curie temperatures T_C^{FM} as high as 200 K have been achieved in bulk (Ge,Mn)Te for Mn concentrations close to the solubility limit of $x_{\text{Mn}} = 0.5$.^{34,169,170} Above this concentration, phase segregation hinders ferromagnetism due to the formation of a hexagonal antiferromagnetic *NiAs-type* MnTe phase, thus dramatically decreasing T_C .^{169–171} On the other side of the phase diagram, reports claimed high Curie temperatures close to 190 K in (Ge,Mn)Te thin films doped with $x_{\text{Mn}} \sim 0.08$ Mn.^{172,173} However, this was later refuted as dilute magnetism and attributed to an inhomogeneous distribution of Mn^{2+} ions due to a spinodal decomposition under specific growth conditions.¹⁷⁴ Moreover, ternary (Ge,Mn)Te grown by *LT-MBE* was found to be dilute only in a narrow window of growth conditions, without the precipitation into secondary phases.¹⁶⁹

In dilute single crystalline (Ge,Mn)Te, T_C has been observed to increase linearly with Mn concentration up to $x_{\text{Mn}} = 0.20$ in (Ge,Mn)Te films. Above this concentration, there is a deviation from the RKKY model,¹⁶⁷ most likely connected with the increasing contribution of an antiferromagnetic coupling between neighboring Mn dopants, characteristic of a MnTe phase,

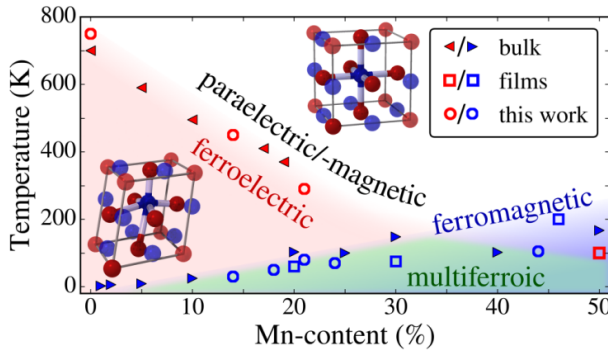


Figure 1.3: Multiferrroic phase diagram of Mn-doped GeTe, extracted from Ref. 129. A multiferrroic phase, combining both ferroelectric and ferromagnetic properties, covers a wide range of compositions, and reaches a maximum T_C of ~ 100 K at $x_{\text{Mn}} \sim 0.3$.

a known antiferromagnet.¹⁶⁷ FM behavior in (Ge,Mn)Te can then be described as a result of competition between the isolated Mn moments which interact ferromagnetically through the polarized charge carriers, and the antiferromagnetic coupling between neighboring Mn moments.¹²⁹

Analogous to GeTe, the ferroelectric moment in (Ge,Mn)Te is a consequence of the rhombohedral distortion and the displacement between Ge (or Mn) and Te sub-lattices. Contrary to Ge atoms, all of the electrons of the half-filled Mn 3d shell contribute to the chemical bonding, and, accordingly, as the Mn content is increased in (Ge,Mn)Te, the rhombohedral lattice distortion is proportionally decreased, up to $x_{\text{Mn}} \approx 0.3$ concentrations, above which the lattice becomes cubic rocksalt.^{129,171} Fig. 1.3, extracted from Ref. 129, draws the (Ge,Mn)Te FE and FM phase diagram, and shows a systematic reduction of the ferroelectric transition temperature T_C^{FE} simultaneous with an increase of ferromagnetic Curie temperature T_C^{FM} as the Mn concentration increases up to $x_{\text{Mn}} = 0.5$. This is consistent with both the decrease of rhombohedral distortion as well as with the increase of Mn magnetic moments density. The overlap between FE and FM phases postulates the possibility for a multiferrroic phase, which manifests in a wide range of compositions, achieving a maximum T_C of 100 K at $x_{\text{Mn}} \sim 0.3$. Additionally, from the phase diagram in Fig. 1.3, a cross-over between both

phases occurs as a function of Mn content, where ferroelectric behavior overtops ferromagnetic behavior below $x_{\text{Mn}} \sim 0.3$, $T_C^{FE} > T_C^{FM}$, and vice-versa above this concentration. Ultimately, the coupling between FE polarization and FM magnetization is mediated by the magnetocrystalline anisotropy, which is related to the rhombohedral lattice distortion of the FE phase.^{175–177}

Ferromagnetic resonance (FMR) studies performed in Ref. 34 describe *two* different magneto crystalline anisotropies for Mn contents $x_{\text{Mn}} = 0.2–0.5$ in Mn-doped GeTe, corresponding to domains with opposing ferroelectric polarizations. In this concentration range, (Ge,Mn)Te is in a cubic crystalline phase, and for a centrosymmetric lattice only *one* FMR resonance would be expected for any magnetic field direction. This translates into two essential properties to the FE phase in (Ge,Mn)Te: (i) although the rhombohedral distortion is negligible (base vectors angles are close to 90°), there is an anion/cation displacement at these concentrations, which breaks inversion symmetry and is required for the FE phase transition, and (ii) the small distortion equally populates crystalline domains with opposing sub-lattice displacement, resulting in the *two* resonances observed.

Also the magnetic anisotropy in (Ge,Mn)Te demonstrates the interplay between sub-lattice displacement and multiferroic properties within these domains, as the easy magnetization axis is parallel to the [111] surface normal up to $x_{\text{Mn}} = 0.2$,¹⁷⁸ rotating towards oblique $\langle 111 \rangle$ at higher concentrations. More importantly for spintronics applications, Przybylinska *et al.*³⁴ observed a varying occupation of these domains upon reversal of the magnetization, demonstrating a coupling between ferroelectric and ferromagnetic properties, and a control of ferroelectric polarization through magnetic fields. Similarly, Krempasky *et al.*³³ further demonstrated electric-field-induced magnetization reversal in this system, opening the door towards an all-electric control of magnetism.

The coexistence of ferromagnetism and ferroelectricity in (Ge,Mn)Te is expressed by the relative entanglement between the FE polarization and FM magnetization directions. Furthermore, both ferromagnetic ordering and ferroelectric symmetry breaking lead to a spin splitting of the electronic bands in the energy and momentum space associated with the combined effects of the Zeeman and Rashba splittings. Fig. 1.4 illustrates how the electronic band structure is

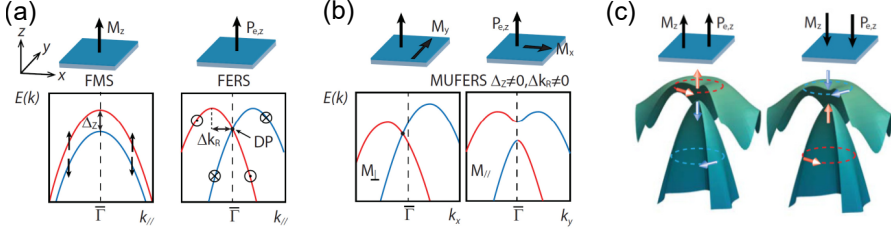


Figure 1.4: Extracted from Ref. 32. Illustration of the Rashba and Zeeman effects on the electronic band structure. (a) Zeeman splitting in a FMS compared to Rashba splitting in a FERS; (b) both Zeeman and Rashba splitting in a MUFERS for different orientations of FE polarization P_e and magnetization M , (c) MUFERS with collinear P_e and M perpendicular to the surface. Different line colors and symbols indicate the expected spin orientations in the bands.

expected to change locally within FMS, FERS and MUFERS. For FMS, the spontaneous magnetization induces a vertical Zeeman splitting of the bands, whereas for FERS the electric polarization induces a Rashba splitting in the $k_{\parallel}$ direction. As illustrated in Fig 1.4, in multiferroic Rashba semiconductors (MUFERS) both effects are entangled with each other, modifying the spin texture as well as the band dispersions. Accordingly, using a simplified Rashba-Zeeman model based on a two-dimensional free-electron approximation (Rashba-Zeeman gas), the Rashba-splitting in the presence of magnetic order can be given by:

$$E_{\pm}(k) = E_0 + \frac{\hbar^2 k^2}{2m^*} \pm \sqrt{\Delta_Z^2 + 4\alpha_R^2 k^2} \quad (1.2)$$

where E_0 is the band edge, m^* the effective electron mass, α_R the k-linear Rashba coupling constant and Δ_Z the momentum-independent Zeeman gap near Γ . Subsequently, a gap Δ_Z can be opened at the Γ -point of the Brillouin zone by any orientation of the magnetization in (Ge,Mn)Te (see Fig. 1.4). However, considering that the spin components in all directions are k -dependent, due to the Rashba-effect, only systems with magnetization *parallel* to the inversion symmetry breaking direction, i.e., $M_z \parallel P_{e,z}$, can reorient the spin of the Rashba electrons and open a gap in all $k_{\parallel}$ directions (cf. Fig. 1.4(c)). The opening of this Rashba-Zeeman gap in the electronic spin-bands has recently been reported using SARPES in (111) epitaxial (Ge,Mn)Te with $x_{\text{Mn}} = 0.13$,³³ where the

multiferroic switching was observed to entangle with the spin helicity as sketched in Fig. 1.4(c).

In summary, the convoluted interplay between local structure and magnetism in (Ge,Mn)Te dictates its multiferroic behavior, and consequently, its functionalization towards spintronic applications. With a multiferroic switching mechanism intimately connected with the relative orientation between **FE** polarization and **FM** magnetization directions, and a low operation temperature, $T_C < 100$ K, **MUFERS** face a few fundamental challenges. At lower Mn concentrations, where a rhombohedral distortion is present, the strong **FE** moment pins the **FM** magnetization, allowing for an effective control of the Rashba-Zeeman splitting.^{33,34,129} This is highly dependent on the rhombohedral distortion in the system, particularly on the displacement between cation and anion sub-lattices, which defines the **FE** polarization direction. On the other hand, the distortion has also a significant influence on the incorporation of Mn atoms, namely on their lattice site within the crystal, also resulting in a displaced site with asymmetric bonds with Te atoms.¹²⁹ The direction of the Mn sub-lattice displacement in (Ge,Mn)Te, together with the orientation of the Mn^{2+} ferromagnetic moment, ultimately defines the magnetization direction. The work described in Ref. 129 reports very different displacements of Ge and Mn atoms in the ferroelectric phase transition, smaller for Mn atoms than for Ge, which have a strong influence on the magnetic properties of (Ge,Mn)Te. A complete understanding of the impact of the Mn sub-lattice displacement on the interplay between the magnetic interaction and the ferroelectric moment is still lacking. This challenge is further exacerbated at higher Mn contents in (Ge,Mn)Te, where the rhombohedral distortion becomes very small, further interweaving the interplay between the sub-lattice displacement, **FE** polarization and **FM** magnetization.

1.4 Current challenges

Based on sections 1.2 and 1.3, the major challenges or goals in the field of ferromagnetic semiconductors can be summarized as follows, for each of the two topical materials introduced above, DMS and MUFERS.

Dilute magnetic semiconductors:

- I. **To increase the Curie temperature** above the current value of 188 K in Mn-doped GaAs. The current understanding of these systems suggests that this goal may be achieved by maximizing substitutional Mn incorporation and hole densities, while minimizing compensating defects.

Multiferroic Rashba semiconductors:

- II. **Understand the interplay between local structure, magnetism and electronic band structure**, in particular, by establishing which fundamental properties influence the ferroelectric polarization, the ferromagnetic behavior and the interplay between them.
- III. **Achieve multiferroic transition temperatures that are compatible with device operation**, by tuning the relevant material properties, such as Mn concentration and strain, or by extending to other magnetic dopants, such as Cr and Fe.

Chapter 2

Objectives and outline

Ever since their discovery, ferromagnetic semiconductors have been regarded as the model systems combining the tunability of semiconductors with the spin contrast of ferromagnets, opening the door to a rich spectrum of outstanding properties and an entirely new set of functionalities. Bridging semiconductor and ferromagnetic properties into a single identity supporting spontaneous spin-polarization up to above room temperature has been the main challenge of the field.

While the list of ferromagnetic semiconductors investigated over the last decades is long, this thesis targets on a fundamental level the role of the local structure of Mn dopants on the functional properties of two representative FMSs of different families: (Ga,Mn)As, a dilute magnetic semiconductor, and (Ge,Mn)Te, a multiferroic Rashba semiconductor.

2.1 Research objectives

The research presented in this thesis is motivated by the open challenges identified in the previous chapter, and was guided by two main objectives one for *dilute magnetic semiconductors*, and another for *multiferroic Rashba semiconductors*.

Dilute magnetic semiconductors:

- **Establish a detailed understanding of the thermal stability of Mn dopants in (Ga,Mn)As and related compounds**, by investigating the diffusion mechanisms responsible for passivation of interstitial Mn and for Mn segregation. The first has a critical role on the ferromagnetic properties of (Ga,Mn)As layers, leading to high Curie temperatures and magnetization. The second, while being detrimental in the context of dilute (Ga,Mn)As, may also enable the realization of hybrid GaAs:MnAs films (with embedded MnAs nanoclusters) with functional properties.

Multiferroic Rashba semiconductors:

- **Characterize with high precision the lattice location of Mn in multiferroic (Ge,Mn)Te thin films**, i.e. the magnitude, direction, and sense of the displacement of the Mn sublattice (i.e. the *magnetic* sublattice) relative to the host Ge and Te sublattices, which is intrinsically linked to the ferroelectric polarization. These properties play a critical role in the Rashba and Zeeman effects, which in turn determine the functional properties of MUFERS.

2.2 Thesis outline

The remainder of this doctoral thesis addresses these objectives, with the first covering *dilute magnetic semiconductors* in chapters 4 to chapter 7, and the second covering *multiferroic Rashba semiconductors* in chapter 8.

Chapter 3 briefly overviews the experimental techniques employed in this research, with particular emphasis on the emission channeling technique.

Chapters 4 to 7 thoroughly investigate the local structure of manganese atoms in (Ga,Mn)As and related compounds, and are presented in the form of *manuscripts*. Chapter 4 studies the lattice site of interstitial Mn in ferromagnetic (Ga,Mn)As, important for the assessment of its out-diffusion for achieving high Curie temperatures. The contents of this chapter are adapted from the published version available in *Applied Physics Letters* **106.1** (2015): 012406.¹⁷⁹ Chapter 5 further addresses the thermal stability of Mn in ferromagnetic (Ga,Mn)As for different concentrations, providing insight on their diffusion mechanisms and their impact on the formation of both high Curie temperature (Ga,Mn)As and hybrid GaAs:MnAs phases. Chapter 6 focuses on the structure and magnetism of both these phases, dilute (Ga,Mn)As and hybrid GaAs:MnAs layers, subjected to different annealing temperatures. Finally, chapter 7 examines the thermal stability of Mn dopants in ferromagnetic Ga-Mn-V layers, providing insight on additional phenomena which mediate the thermal processes and Mn diffusion in semiconductors closely related to (Ga,Mn)As.

Chapter 8 delves into the local structure of multiferroic Rashba semiconductor (Ge,Mn)Te, investigating the lattice location of Mn in GeTe and (Ge,Mn)Te. This chapter details the study of the sub-lattice displacement of Mn dopants in these semiconductors, providing insight on its fundamental role in the multiferroic properties of these materials.

The last chapters, chapter 9 and chapter 10, present an overarching discussion of the results, in the broader perspective of the the field of ferromagnetic semiconductors, and closing this thesis with a contextualized outlook on its future.

Chapter 3

Experimental techniques

The work described in this thesis explored the local structure and magnetism of ferromagnetic semiconductors using several experimental techniques. This chapter describes the sample preparation (section 3.1) and characterization (section 3.2). The latter section is divided between the various techniques utilized: emission channeling (EC), synchrotron radiation x-ray diffraction (XRD), extended x-ray absorption fine structure (EXAFS), and superconducting quantum interference device (SQUID) magnetometry. Since all experiments followed standard experimental procedures and protocols, only short descriptions are presented.

3.1 Sample preparation

3.1.1 Dilute magnetic semiconductors

The samples utilized in the experiments detailed in Chapters 4 to 7 were grown in the University of Nottingham, using low-temperature molecular beam epitaxy (LT-MBE) and following the procedures outlined in Ref. 59. The ferromagnetic thin films of (Ga,Mn)As, (Ga,Mn)(As,P) and (Ga,Mn)(As,Sb) described in

Chapters 4 and 7 were grown on GaAs (100) substrates, up to ~ 20 nm in thickness, with a concentration of 6% Mn. The (Ga,Mn)Sb films were grown to similar specifications but on GaSb substrates. On the other hand, the (Ga,Mn)As samples detailed in Chapter 5 and 6 were grown under different specifications for each concentration: the 1% Mn samples were grown on GaAs substrates with a thickness of $1.5 \mu\text{m}$, and the 5% Mn samples on AlAs buffer layers on GaAs substrates, with a 200 nm thickness. The experiments in the ultra-dilute regime were performed in GaAs, GaP and GaSb substrates.

3.1.2 Multiferroic Rashba semiconductors

The samples utilized in the experiments detailed in Chapter 8 were grown in the Johannes Kepler Universität Linz, using molecular beam epitaxy () and following the procedures outlined in Refs. [129, 169, 170]. The epitaxial (Ge,Mn)Te films were grown with Mn concentrations up to 21% and a thickness of 500 nm on $\text{BaF}_2(111)$ substrates at 280°C .^{169, 170}

3.2 Sample characterization

3.2.1 Emission Channeling

Emission channeling (EC) is used to study the lattice location of dopants or impurities in single crystals, with the aim of analysing their influence on local structure and electronic/magnetic properties of the material. The principle of emission channeling differs from conventional channeling techniques that rely on external ion beams and their interaction with the dopant/impurity atoms in the host lattice, such as Rutherford backscattering spectrometry (RBS). In emission channeling, the channeled particles are emitted from *within* the crystal by radioactive isotope probes of the element under study.

The emission channeling technique makes use of charged particles, either α or electron emitters (β^- or conversion electrons), emitted isotropically by a decaying radioactive isotope previously implanted in a single crystal layer. These

emitted high-energy particles are then channeled along the screened Coulomb potential of atomic rows and planes and recorded by a position sensitive detector as a function of angle towards major crystallographic directions. Along low-index crystal directions of single crystals, this anisotropic scattering results in well-defined channeling or blocking effects which are strongly dependent on the initial position of the emitted particles and represent characteristic emission patterns for the corresponding lattice site.¹⁸⁰

A direct comparison between experimental and calculated two-dimensional emission patterns results in a quantitative lattice location. Due to the small amounts of radioactive probes that are required to be introduced in the target material, emission channeling is more sensitive to low dopant concentrations in crystals than conventional implementations of ion-channeling techniques. This is particularly attractive for dilute systems, such as the ones studied in this thesis.

A typical emission channeling experiment can be summarized in four steps: (1) the single crystal or epitaxial thin film is implanted with a radioactive isotopes; (2) a fraction of emitted charged particles are channeled along the crystal axes and planes, describing anisotropic emission patterns; (3) these patterns are recorded using a position-sensitive detector around selected crystallographic axes; and (4) the lattice site(s) of the dopants/impurities is determined through fitting these patterns by accurate theoretical two-dimensional emission distributions for a variety of possible lattice sites. The remainder of this section will briefly go through these steps in order to provide the reader with a general view of emission channeling, to which, however, some details of particular relevance for this thesis have been added. For more details than present on this thesis, the reader is referred to Refs. 180–184.

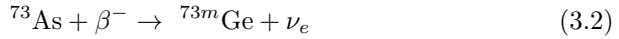
3.2.1.1 Isotope implantation

The emission channeling experiments presented throughout this thesis were performed at the on-line isotope separator facility ISOLDE at CERN,¹⁸⁴ and used mostly the radioactive isotope ^{56}Mn , supplemented by some studies applying ^{73}As . All ^{56}Mn experiments were performed on-line, where both

implantation and measurement are performed *in-situ*, making use of the Emission Channeling – Short Lived Isotopes (EC-SLI) setup.¹⁸⁴ ^{56}Mn has a half life of 2.56 hours and is a β^- emitter with the following decay mode:



^{73}As experiments, presented in chapter 5, were performed *ex-situ* utilizing a setup better adjusted to the decay rate of longer lived isotopes (cf. Ref. 185). ^{73}As has a half life of 80 days and decays by electron capture to the metastable excited state ^{73m}Ge (499 ms), whose de-excitation into the ground state of ^{73}Ge is accompanied by the emission of conversion electrons:



The implantation of these radioactive probes followed standard protocols of ion implantation: the atoms or molecules were ionized at the ion source, accelerated by an electrostatic field generated by a high-voltage electrode (tens of kV), mass-separated by an analyzing magnet, and electromagnetically steered into the target material.

The ion bombardment produces a variety of lattice defects, such as self-interstitials and vacancies, which plays a role in the lattice location of the radioactive probes. Typical emission channeling implantation fluences are low ($10^{12} - 10^{13} \text{ cm}^{-2}$). As an example, the implantation of ^{56}Mn probes at 50 keV under a 10° angle results in a total of 1000 displacements per impinging ion. Albeit a significant amount of defects is produced, the dynamic annealing of these defects during implantation decreases their concentration within the implanted layer. Nevertheless, the potential effect of such defects on the lattice sites occupied by the radioactive implanted probes must be taken into consideration when interpreting EC data. For example, in section 7.6 we observe the conversion from interstitial to substitutional Mn, which is likely enabled or at least enhanced by the vacancies produced during implantation. Moreover, in almost all experiments, a random fraction is observed in the as-implanted state,

which at least partially decreases upon thermal annealing. This contribution is typically attributed to probes located in regions which became highly disordered upon formation (and possibly aggregation) of implantation-induced defects, and is further discussed in section 3.2.1.3.

3.2.1.2 Theoretical considerations

Quantitative lattice location of the radioactive probes is obtained by fitting the calculated emission patterns to experimental ones. Using the *manybeam* software, developed by Hofsäss and Lindner^{180–182} and modified by Wahl,¹⁸³ theoretical angle-dependent channeling yields can be in principle calculated for any emitter lattice position along any crystallographic direction. The emission patterns are typically calculated within an angular range of 3° once the crystallographic direction has been introduced into the source code of the program.

Manybeam calculations start from the crystallographic structure of the host material, which can be experimentally determined by x-ray diffraction measurements, and is typically well established for most conventional semiconductors investigated in this thesis. The *manybeam* formalism uses two-dimensional projections with respect to the channeling axes, obtained from the 3-dimensional structures published in literature. Another important input parameter is the vibration amplitude of the crystal atoms, portrayed as the one-dimensional projected root mean square (rms) vibration amplitude u_1 . This can be determined experimentally from the Debye-Waller factors in x-ray or neutron diffraction experiments. Published values are used as input for the *manybeam* calculations.

The output of the *manybeam* calculations is a two-dimensional emission pattern library compiling various dopant/impurity lattice sites and rms displacements u_1 , associated with each given material, channeling axis and radioactive isotope. In addition, these patterns are *smoothed* using a Gaussian with $\sigma \simeq 0.1^\circ$ to account for the contribution of the 1 mm beam spot to the experimental angular resolution ($\sigma \approx 0.16^\circ$ for typical EC experiments). Higher values of σ may be used to account for crystal mosaicity and extended damage due to high

fluence implantation.¹⁸⁶ Furthermore, 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 theoretical emission pattern $\chi^{theo}(\theta, \phi)$. As an example, Fig. 3.1 shows the simulated emission patterns for ^{56}Mn , in different sites of the GaAs zincblende structure, around different crystallographic directions. Patterns calculated for the $\langle 111 \rangle$ direction cannot distinguish between any of the sites S_{Ga} , S_{As} , T_{Ga} and T_{As} , as illustrated in the figure by equivalent patterns. $\langle 100 \rangle$ patterns are unable to distinguish between S sites and T sites, i.e. S_{Ga} from T_{As} , and S_{As} from T_{Ga} . In contrast, patterns calculated for $\langle 110 \rangle$ and $\langle 211 \rangle$ directions clearly demonstrate the difference in emission yields in between S_{Ga} and S_{As} , and in between T_{Ga} and T_{As} : due to the lack of mirror symmetry of the $\langle 110 \rangle$ and $\langle 211 \rangle$ directions the left-right asymmetries of the patterns allow for a clear identification of the different lattice sites.

3.2.1.3 Fitting procedures

Emission channeling patterns are analyzed by fitting the experimental data with the theoretical *manybeam* simulations described previously. For this purpose, we employ the *FDD* program, developed by U. Wahl,¹⁸⁷ to perform the quantitative analysis of the experimental two-dimensional patterns $\chi^{exp}(\theta, \phi)$. This software uses a χ^2 -minimization fitting procedure to fit a linear combination of the calculated yields $\chi^{theo}(\theta, \phi)$ to the experimental patterns:

$$\chi^{exp}(\theta, \phi) = S \left[f_{rand} + \sum_{i=1}^n f_i \chi_i^{theo}(\theta, \phi) \right] \quad (3.4)$$

where S is a scaling factor, f_i denotes the fraction of emitter atoms occupying the i^{th} site, and n the number of sites considered in the fit. The random fraction f_{rand} accounts for emitter atoms which do not contribute significantly to the anisotropy of the pattern, and can be located either on sites with very low crystal symmetry or in heavily damaged (or even amorphous) surroundings.

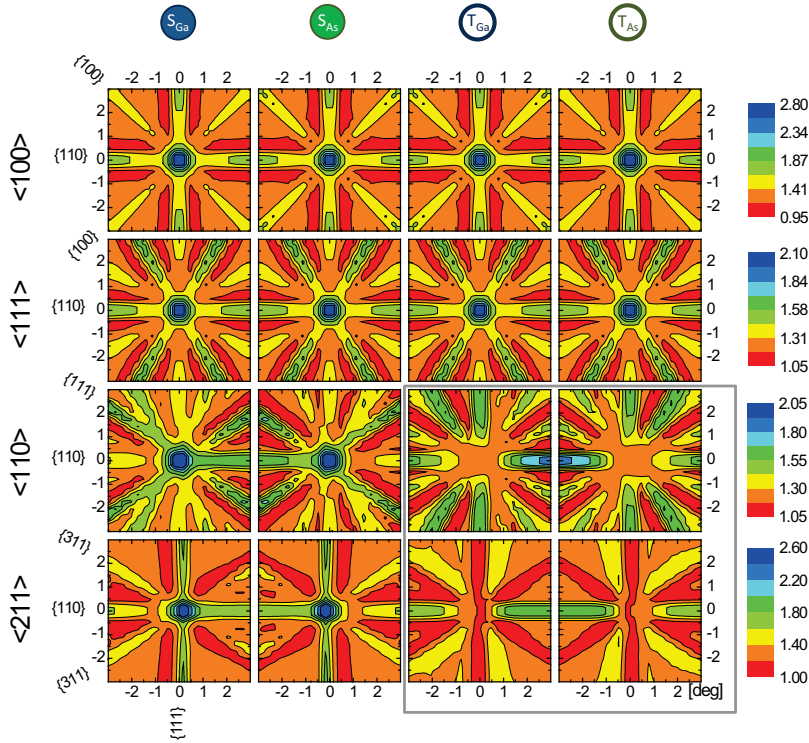


Figure 3.1: Figure extracted from Ref. 90. Simulated channeling patterns for ^{56}Mn , β^- emitter, on substitutional Ga sites (S_{Ga}), substitutional As sites (S_{As}), and the two T interstitial sites (T_{As} and T_{Ga}) in the GaAs zincblende structure. The marked simulations allow for a clear distinction between T_{As} and T_{Ga} patterns.

Because the sum of all the fractions must amount to 1, f_{rand} is given by

$$f_{\text{rand}} = 1 - \sum_{i=1}^n f_i. \quad (3.5)$$

Using non-linear least squares fitting routines, FDD determines the best fit values of S , f_i , x_0 , y_0 and ϕ_0 simultaneously. x_0 and y_0 are the coordinates of the channeling axis on the detector plane (i.e. the “center” of the pattern) and ϕ_0 is an azimuthal rotation angle of the pattern with respect to the channeling

axis. S , x_0 , y_0 and ϕ_0 are always allowed to vary in order to provide correct normalization of the experimental pattern and to achieve optimum translational and azimuthal orientation with respect to the detector. Finally, only up to three different sites are typically considered in the fit, as the fitting routine loses sensitivity with increasing number of sites.

3.2.1.4 Scattered electron background correction

A final aspect to take into consideration in an emission channeling experiment is the background contribution from stray detected electrons. Two types of electrons reach the detector, *direct* and *scattered* electrons. *Direct* electrons are those with initial direction in the vicinity of the detection axis, while *scattered* electrons are initially not emitted towards the detector, but still reach it after scattering under a large angle. The number of *direct* electrons is roughly 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.

The number of detected electrons is, however, always larger than this estimate, due to the additional electrons, which scatter from inside the sample, by the host atoms, or outside the sample, by setup parts. These *scattered* electrons constitute an additional isotropic background in the experimental emission yields, and cannot be taken into account in the theoretical framework of channeling implemented in the *manybeam* program.

This problem can be corrected by the introduction of a background correction factor, which determines the ratio between the total number of electrons that arrive at the detector and direct electrons. This background correction factor can be estimated using the computer program *Pad* based on the Geant4 toolkit,^{188,189} using the Monte-Carlo method. *Pad* simulates the propagation of electrons emitted from the sample and, among the ones that reach the detector, distinguishes the direct from the scattered ones. This requires detailed input information: the sample's geometry and composition, the β^- decay energy spectrum (isotope-specific) and the exact geometry of the setup, i.e. the position, shape and composition of the setup parts.

Estimated background correction factors for the experiments in this thesis range from 1.7 for ^{56}Mn experiments on III-Mn-V experiments to 2.1 for ^{56}Mn experiments on (Ge,Mn)Te crystals.

A second source of background are γ -rays, which are emitted by most radioactive isotopes, and may also be counted in the detector, though generally with less efficiency than electrons. The contribution of γ -rays can be estimated by means of closing a valve in front of the detector and comparing the count rates with valve open and closed.

The isotope used for most measurements in this thesis, ^{56}Mn , has three major gamma lines with energies of 847 keV (branching ratio 99%), 1811 keV (27%) and 2113 keV (14%), which are highly penetrating. The background count rate in the detector resulting from such gammas varies somewhat for different experiments, in accordance with how well it was possible to focus the ^{56}Mn beam through a 1 mm collimator onto the sample (part of the gamma background results from activity deposited on the collimator), but generally amounts to 10-20% of the total count rate.

3.2.2 Synchrotron radiation x-ray diffraction

X-ray diffraction experiments provide information on the crystallographic properties of a sample. Among possible experimental geometries, the most commonly used is the θ - 2θ Bragg-Brentano geometry, where the sample is tilted towards an incoming x-ray beam over an angle θ and the detector is positioned at an angle 2θ . For this geometry, the Bragg diffraction criterion is fulfilled for atomic planes parallel to the sample stage and separated by a distance d , matching n times the x-ray wavelength λ , $2d \sin \theta = n\lambda$. In crystalline samples this geometry results in intense peaks corresponding to crystallites whose atomic planes are parallel to the sample surface, while not accessing information on crystalline domains oriented in oblique directions.

Regarding the source of x-rays, one can distinguish between conventional laboratory sources and synchrotrons. Synchrotron facilities are typically well equipped to perform a variety of high-resolution measurements, and have the

added advantage of having a brilliance that is several orders of magnitude larger than a standard laboratory source.^a Higher brilliance is advantageous for the detailed characterization of dilute and complex systems such as the ones investigated in this thesis: on the one hand, the higher brightness allows in general to probe smaller amounts of material; on the other hand, the higher brilliance allows for higher collimation (angular resolution) while maintaining a sufficiently high beam intensity.

Considering crystalline samples grown on crystalline substrates, such as the ones utilized in this thesis, the intensity of the resulting characteristic x-ray peaks is approximately proportional to the layer thickness (as long as the thickness is significantly smaller than the x-ray absorption length). In other words, when the film thickness is significantly smaller than the absorption length, the diffraction peak for the substrate will be orders of magnitude larger than for a film on top of it. This is particularly important for the structural characterization and identification of secondary-phases embedded in a single crystal on a substrate, as is the case investigated in chapter 6. In order to probe the secondary-phases embedded on epitaxial thin films, we resorted to a grazing incidence X-ray diffraction (GI-XRD) geometry, where the sample is irradiated by x-rays at a small angle, which has two advantages: it reduces the x-ray penetration in the substrate, maximizing the diffraction from thin film; the Bragg condition is not fulfilled for the substrate peaks, resulting only in contributions from the x-rays diffracted from the secondary phases which are not aligned with the host lattice.

3.2.3 Extended x-ray absorption fine structure

X-ray absorption spectroscopy (XAS) is the measurement of the x-ray absorption coefficient of a material as a function of x-ray energy. A sample is irradiated with x-rays of narrow line width, a fraction of which will be absorbed by the material, depending on the sample's absorption coefficient, thickness, and type of atoms which constitute it. When the incident x-ray energy surpasses the binding energy of an electron to the target atom, the number of absorbed x-rays

^aBrilliance describes both the brightness and the angular spread of the beam.

increases dramatically, resulting in an absorption edge. These absorption edges are characteristic to each element on the periodic table, due to the different binding energies of its electrons, giving **XAS** element selectivity.

When an incident photon is absorbed, the atom ejects a core photoelectron, leaving behind a core hole. The ejected photoelectron interacts with the electrons in the surrounding atoms, creating an interference pattern in the absorption spectra. Extended x-ray absorption fine structure (**EXAFS**) investigates the resulting oscillatory structure which extends hundreds of electron volts past the edge. This fine structure contains information on the atomic neighborhood of the probed element within the sample, making it possible to infer on its chemical coordination environment, i.e. how many neighboring atoms, of which elements, and at what distance.

3.2.4 Superconducting quantum interference device magnetometry

A superconducting quantum interference device (**SQUID**) is a very sensitive magnetometer typically used to measure extremely small magnetic fields. This device operates by moving a magnetic sample through superconducting loops containing Josephson junctions. Superconducting wires connect detection coils to the device in a closed loop, allowing for an electric current to be induced and measured as a sample moves through the coils. Changing the magnetic flux in the detection coils changes the persistent current in the circuit, which is proportional to the magnetic moment of the sample.

In a calibrated system, **SQUID** magnetometers provide highly accurate measurements of the magnetic moment of the sample (with a resolution down to 10^{-8} emu). However, at this sensitivity regime, magnetic contamination and measurement artifacts must be carefully taken into account, typically for a magnetization below 10^{-4} emu. This is the case for some of the ferromagnetic semiconductors investigated in this thesis (cf. chapter 6), in which carefully designed protocols and procedures were followed, ensuring the minimization of contamination and other magnetic artifacts.¹⁹⁰ Thin

ferromagnetic semiconductor films ($< 1 \mu\text{m}$), particularly at low dopant concentrations, display small magnetic moments. The magnetic moment of a typical sample can be between 10^{-7} and 10^{-4} emu (10^{-10} and 10^{-7} A m²), thus requiring the high sensitivity of a **SQUID** magnetometer.

Chapter 4

Identification of the interstitial Mn site in ferromagnetic (Ga,Mn)As

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4.1 Abstract

We determined the lattice location of Mn in ferromagnetic (Ga,Mn)As using the electron emission channeling technique. We show that interstitial Mn occupies the tetrahedral site with As nearest neighbors (T_{As}) both before and after thermal annealing at 200°C, whereas the occupancy of the tetrahedral site with Ga nearest neighbors (T_{Ga}) is negligible. T_{As} is therefore the energetically favorable site for interstitial Mn in isolated form as well as when forming complexes with substitutional Mn. These results shed new light on the long standing controversy regarding T_{As} versus T_{Ga} occupancy of interstitial Mn in (Ga,Mn)As.

4.2 Introduction

(Ga,Mn)As has become the model system to explore the physics of carrier-mediated ferromagnetism in semiconductors and the associated spintronic phenomena.^{5,39} In particular, as the most widely studied dilute magnetic semiconductor (DMS), (Ga,Mn)As is the perfect example of how the magnetic behavior of DMS materials is strongly influenced by local structure. In typical high Curie temperature (Ga,Mn)As thin films (several % Mn regime), the majority of the Mn atoms substitute for Ga (Mn_s), while a minority fraction (several % of all Mn) occupies interstitial sites (Mn_i).^{29,51} Mn_s provides both the localized magnetic moment and the itinerant hole that mediates the magnetic coupling, whereas Mn_i has a twofold compensating effect: (i) magnetically, as Mn_i - Mn_s pairs couple antiferromagnetically, and (ii) electrically, since double donor Mn_i compensates Mn_s acceptors.²⁹ For a given Mn_s concentration, Mn_i therefore determines the hole concentration, the Fermi level and the effective Mn_s concentration (of non-compensated Mn_s moments), all of which define the magneto-electronic behavior of (Ga,Mn)As. The existence of such a crucial role of Mn_i is clearly reflected in the effect of the Mn_i concentration on the two relevant figures of merit: Curie temperature (T_C) and magnetization.^{25,29,51}

Despite this central role in the understanding of (Ga,Mn)As, and consequently

of Mn-doped III-V [DMS](#) materials, interstitial Mn is far from being a well understood defect. The presence of Mn_i in ferromagnetic (Ga,Mn)As was first reported based on ion channeling measurements.⁹² Although consistent with Mn_i occupying tetrahedral (T) interstitial sites, the measurements did not allow to discriminate between the two nonequivalent T sites: coordinated by four Ga atoms (T_{Ga}) or by four As atoms (T_{As}). Transmission electron microscopy ([TEM](#)) measurements using the (002) diffracted beam indicated that Mn_i predominantly occupies the T_{As} site.⁵⁵ X-ray absorption fine structure ([XAFS](#)) techniques were later applied, suggesting T_{Ga} occupancy (e.g. Refs. [95, 96]). However, [XAFS](#) is not well suited to distinguish neighboring elements with similar atomic numbers, as is the case for Ga and As, especially in such cases of multi-site occupancy (substitutional and interstitial) where the site to be identified is in fact the minority one (interstitial). In pioneering work using X-ray scattering techniques to probe dopant lattice location, comparable T_{Ga} and T_{As} occupancies have been reported.^{97–99} Coexisting T_{Ga} and T_{As} occupancies would suggest that the Mn_i lattice site depends on the presence of neighboring Mn_s atoms, i.e. that isolated Mn_i and Mn_i in Mn_i - Mn_s pairs occupy different T sites. This is however in contradiction with density functional theory ([DFT](#)) calculations which predicted that, for typical ferromagnetic (Ga,Mn)As samples (where the Mn_s concentration is significantly larger than that of Mn_i), T_{As} is the most stable site for Mn_i regardless of being isolated, in Mn_i - Mn_s pairs, or even in Mn_s - Mn_i - Mn_s triplets.⁶⁵ Solving this inconsistency would allow for a better understanding of the mechanisms of electric and magnetic compensation by Mn_i which, as introduced above, plays a central role in the behavior of (Ga,Mn)As.

Using the emission channeling (EC) technique, we show here that interstitial Mn occupies only T_{As} sites in ferromagnetic, high Curie temperature (Ga,Mn)As thin films. The EC technique makes use of the charged particles emitted by a decaying radioactive isotope. The screened Coulomb potential of atomic rows and planes determines the anisotropic scattering of the particles emitted isotropically during decay. Along low-index crystal directions of single crystals, this anisotropic scattering results in well-defined channeling or blocking effects. Because these effects strongly depend on the initial position of the emitted

particles, they lead to emission patterns which are characteristic of the lattice sites occupied by the emitting probe atoms. We have previously applied the EC technique to determine the lattice location of Mn in GaAs in the ultra-low doping regime ($< 0.05\%$ Mn).^{90,94} With emission channeling, the unambiguous distinction between T_{Ga} versus T_{As} sites in the GaAs (zincblende) lattice is a direct structural consequence of the mirror-asymmetry of selected crystal axes (typically $\langle 211 \rangle$ or $\langle 110 \rangle$).⁹⁰

4.3 Experimental details

We report on two separate experiments on the lattice location of radioactive ^{56}Mn (half-life $t_{1/2} = 2.56$ h) implanted into (Ga,Mn)As thin films grown by molecular beam epitaxy (LT-MBE).⁵⁹ Experiment A consisted of implanting a $\text{Ga}_{0.94}\text{Mn}_{0.06}\text{As}$ thin film (25 nm thick, grown directly onto the GaAs substrate) with ^{56}Mn to a fluence of $2 \times 10^{12} \text{ cm}^{-2}$, at an energy of 40 keV, and a beam angle of 60° with respect to the surface normal. The high implantation angle was chosen in order to maximize the fraction of ^{56}Mn probes implanted in the (Ga,Mn)As thin film. The near-Gaussian depth profile simulated using SRIM-2008¹⁹¹ is characterized by a peak concentration of $6.2 \times 10^{17} \text{ cm}^{-3}$ (≈ 0.003 atomic %, i.e. negligible increase in Mn concentration), a projected range (average depth) of 17 nm and a straggling of 11 nm, with an estimated $< 27\%$ of the ^{56}Mn probes implanted into the GaAs substrate. Experiment B consisted of implanting a $\text{Ga}_{0.95}\text{Mn}_{0.05}\text{As}$ thin film (200 nm thick, grown onto a 200 nm AlAs buffer layer, on a GaAs substrate) with ^{56}Mn to a fluence of $7 \times 10^{12} \text{ cm}^{-2}$, with an energy of 30 keV and an angle of 17° (resulting in a peak concentration of $2.4 \times 10^{18} \text{ cm}^{-3}$, a projected range of 21 nm and a straggling of 11 nm, i.e. with all the ^{56}Mn within the film). In order to monitor the degree of disorder upon implantation of the radioactive probes and subsequent annealing, we also determined the lattice location of As using radioactive ^{73}As ($t_{1/2} = 80$ d) – experiments C and D. These experiments consisted of implanting a thin film as in experiment B with ^{73}As to a fluence of $5 \times 10^{13} \text{ cm}^{-2}$, with an energy of 50 keV and an angle of 10° (resulting in a peak concentration of $1.5 \times 10^{19} \text{ cm}^{-3}$, a projected range of 26 nm and a

straggling of 13 nm, i.e. with all the ^{73}As within the film). Both ^{56}Mn and ^{73}As were implanted at room temperature, at the on-line isotope separator facility ISOLDE at CERN. Emission channeling measurements were carried out in the as-implanted state and after annealing at 200°C: in air for 3 hours in experiments A and C; in vacuum ($< 10^{-5}$ mbar) for 10 min in experiments B and D. Angular-dependent emission patterns were recorded along various crystallographic axes using a position- and energy-sensitive detection system similar to that described in Ref. 185. Experiments A and B (with relatively short-lived ^{56}Mn) were performed on-line using the EC-SLI setup;¹⁸⁴ experiments C and D (the longer-lived ^{73}As) were performed off-line.¹⁸⁵ In experiments B, C and D, four axes were measured ($\langle 100 \rangle$, $\langle 111 \rangle$, $\langle 110 \rangle$ and $\langle 211 \rangle$), typical of emission channeling experiments on host semiconductors with cubic structure (cf. e.g. Refs. [90, 94]). In experiment A, the measurements were limited to the $\langle 211 \rangle$ axis, which as will be shown below is sufficient to unambiguously determine the site occupancy (at least when combined with experiment B, where all four axes were measured). The implantation parameters, film thickness and annealing time of experiment A were carefully chosen to allow us to determine the lattice site(s) occupied by Mn_i in a stage of annealing for which the Mn_i fraction would have decreased to half of the as-grown/as-implanted value (based on magnetometry measurements). The theoretical emission patterns for probes occupying possible lattice sites are calculated using the many-beam formalism for electron channeling in single crystals.¹⁸⁰ The lattice location was quantitatively determined by fitting the experimental patterns with theoretical ones using the two-dimensional fit procedure outlined in Ref. 192. More details onto the experimental approach and data analysis, including a description of the lattice sites and how they can be unambiguously distinguished with emission channeling, can be found in Ref. 90. Other examples of emission channeling studies using short-lived isotopes of transition metals can be found in the following Refs. [193–195] for Mn, [194, 196] for Co, and [184, 197] for Ni.

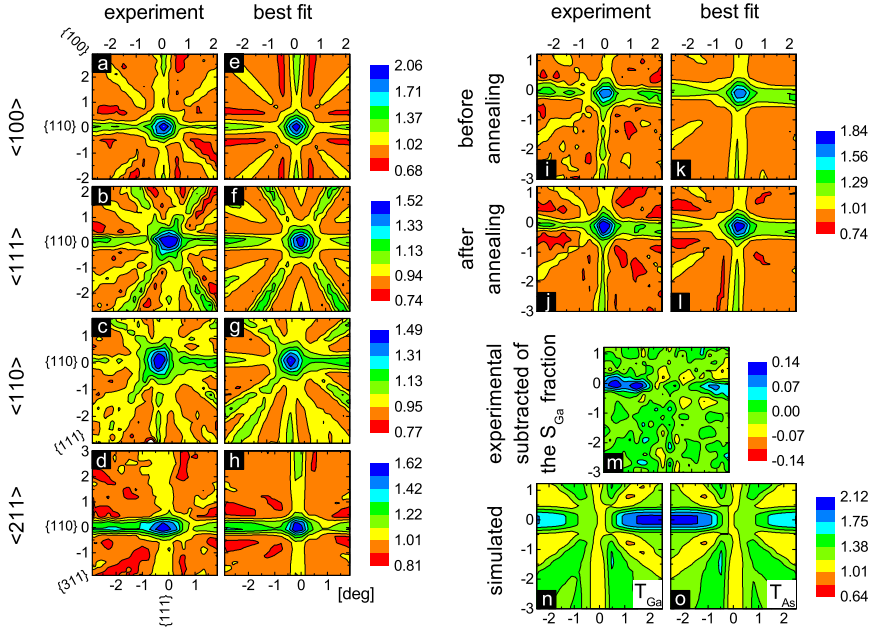


Figure 4.1: (Color online) (a-d) Experimental β^- emission patterns of experiment B after thermal annealing (10 min, in vacuum), along the four measured directions, and best fits of theoretical patterns (e-h). The best fit is obtained for 71% of the ^{56}Mn atoms on S_{Ga} (Mn_s) and 25% on T_{As} (Mn_i) sites. (i, j) Experimental patterns and best fit (k, l) for experiment A (only the $\langle 211 \rangle$ direction), before and after annealing (3 h, in air). The best fits are obtained for 64/77% of the ^{56}Mn atoms on S_{Ga} (Mn_s) and 25/15% on T_{As} (Mn_i) sites before/after annealing. (m) Experimental pattern [of Fig. (j)] after subtraction of the fitted S_{Ga} component. (n, o) Simulated patterns for ^{56}Mn on T_{Ga} and T_{As} sites, respectively.

4.4 Results

As a representative example, Fig. 4.1 (a-h) shows the experimental β^- emission patterns of experiment B after thermal annealing (10 min, in vacuum), along the four measured directions (a-d), as well as the best fits to the theoretical patterns (e-h). Similarly, Fig. 4.1 (i-l) compares experimental patterns (i,j) and best fit (k,l) for experiment A (only the $\langle 211 \rangle$ direction), both before and after annealing (3 h, in air). Fig. 4.1 (m-o) qualitatively illustrates how the mirror asymmetry of the $\{110\}$ -planar channeling measured in the vicinity of the $\langle 211 \rangle$ direction (horizontal plane in the figure) allows us to distinguish between T_{As} and T_{Ga} sites: after subtracting from the experimental data the fitted component occupying substitutional Ga (S_{Ga}) sites, the asymmetry of the residual $\{110\}$ -planar channeling corresponds to that of T_{As} , i.e. stronger channeling on the left versus right in the Fig., which is the opposite of T_{Ga} . Quantitative analysis is provided by numerically fitting the data to calculated patterns, as mentioned above, from which the fractions of ^{56}Mn atoms in the different lattice sites are obtained - compiled in Fig. 4.2 (top) for experiments A and B.

Figure 4.2 (bottom) illustrates the technique's sensitivity specifically for the case of T_{As} versus T_{Ga} occupancy, by showing for experiment A (after annealing) the error associated with the fit (χ^2) as the fractions on T_{As} and T_{Ga} sites are varied in the vicinity of the best fit values (15% for T_{As} and 0% for T_{Ga} , with χ_0^2), leaving all other fit parameters free. The black line contour corresponds to $\chi^2 - \chi_0^2 = 1$, giving standard deviations of 2% for the T_{As} fraction and of 0.5% for T_{Ga} . Note that the percentages are with respect to all the ^{56}Mn , i.e. even if there is indeed T_{Ga} occupancy within the technique's sensitivity, it is for all purposes negligible. Vanishing T_{Ga} occupancy (with comparable standard deviation) is found both before and after annealing, both in experiments A and B.

Before discussing in detail the T_{As} versus T_{Ga} occupancy, we make three relevant observations. First, while the interstitial Mn fraction is unaffected by the 10 min vacuum annealing (experiment B), annealing for 3 hours in air decreases it by almost a factor of 2. This is consistent with our complementary magnetometry measurements (cf. section 4.6), and with the Mn_i annealing kinetics previously

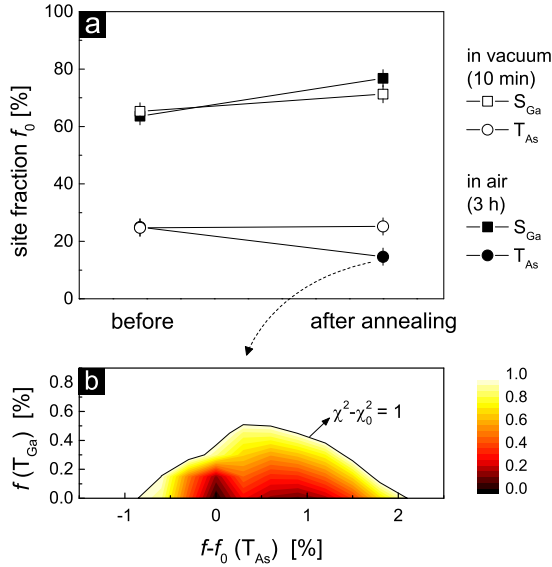


Figure 4.2: (Color online) Top - Fractions of ^{56}Mn atoms on S_{Ga} and T_{As} sites in experiments A and B. Bottom - Error associated with the fit $\chi^2 - \chi_0^2$, with χ_0^2 being the value for the best fit, for experiment A after annealing, as the fractions f on T_{As} and T_{Ga} sites are varied in the vicinity of the best fit values f_0 (15% for T_{As} and 0% for T_{Ga}), leaving all other fit parameters free. The black line contour corresponds to $\chi^2 - \chi_0^2 = 1$.

reported based on transport and magnetometry measurements.^{29,60} Second, in both experiments A and B, we observe an increase in substitutional fraction upon annealing, which we attribute to the recovery of disordered regions (created upon implantation), rather than interstitial Mn being converted to substitutional. This is confirmed by experiments C and D, where we see a comparable increase of the substitutional As fractions (cf. section 4.6). Third, it is important to note that the determined site-fractions correspond to the implanted radioactive ^{56}Mn probes, which are not necessarily (and most likely are not) the same as those of the stable ^{55}Mn atoms incorporated during LT-MBE growth. The goal of these experiments was not to determine the absolute fraction of interstitial Mn in (Ga,Mn)As, but to evaluate the stability of the possibly occupied interstitial sites, which we discuss next.

4.5 Discussion and conclusion

The main finding here is that interstitial Mn occupies only T_{As} sites, with negligible (if any) T_{Ga} occupancy. In terms of the local structure of Mn_i (in T_{As} sites), there are essentially three possible situations to consider (Fig. 4.3): isolated Mn_i (coordinated by As and Ga in the first and second neighbor shell), Mn_i - Mn_s pairs (with a Mn_s substituting one of the Ga atoms in the second neighbor shell), and Mn_s - Mn_i - Mn_s triplets (with two Mn_s substituting Ga atoms in the second neighbor shell). The effect of larger complexes (e.g. $3Mn_s$ - Mn_i) can be neglected since the fraction of substitutional Mn in such configurations is significantly smaller than those considered (11% for $3Mn_s$ and even smaller for larger complexes, assuming random Mn distribution).¹⁹⁸

The thermal stability, i.e. the activation energy for diffusion E_a , increases from isolated Mn to Mn_i - Mn_s pairs to Mn_s - Mn_i - Mn_s triplets.⁶⁵ $E_a = E_m$ for isolated Mn, with E_m being the effective migration barrier in a T_{As} - T_{Ga} - T_{As} path; $E_a = E_m + E_b$ for Mn_i - Mn_s pairs and Mn_s - Mn_i - Mn_s triplets, with E_b being the binding energy of the complexes, which is larger for Mn_s - Mn_i - Mn_s triplets due to the Coulomb interaction between ionized Mn_i donors and Mn_s acceptors (one/two Mn_s for pairs/triplets). Since the ^{56}Mn probes are randomly distributed upon implantation, and long range diffusion of Mn_s and Mn_i is suppressed at room temperature, we can expect the largest fraction of isolated Mn_i in the as-implanted state. At 200°C, Mn_i is mobile and, therefore, isolated Mn_i and Mn_i in Mn_i - Mn_s pairs progressively populate the Mn_s - Mn_i - Mn_s configuration (with the dissociation of Mn_i from Mn_s - Mn_i - Mn_s triplets being the limiting reaction for long-range diffusion of Mn_i). Since we observe vanishing T_{Ga} occupancy both before and after annealing, we can conclude that the T_{As} site is the most stable site regardless of Mn_i being isolated, in Mn_i - Mn_s pairs or in Mn_s - Mn_i - Mn_s triplets. In other words, regardless of the Mn_s coordination, the migration path of Mn_i between neighboring T_{As} and T_{Ga} sites is asymmetric, with T_{As} being the lower energy side. This picture is in qualitative agreement with previous *ab initio* calculations for the different coordination configurations.⁶⁵ An experimental assessment of the different energy barriers at play requires a detailed investigation of the lattice location

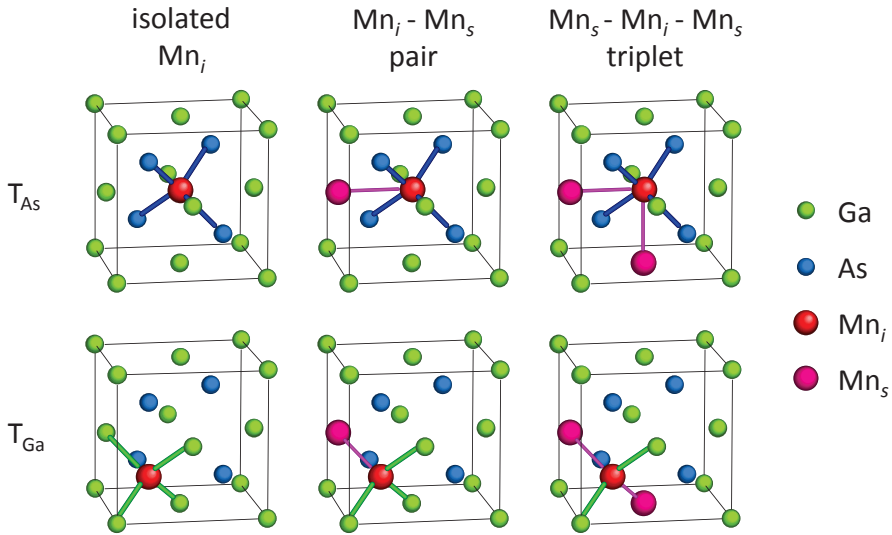


Figure 4.3: (Color online) Representation of the relevant Mn_i sites and coordination: in T_{As} (top) and T_{Ga} (bottom) sites, for isolated Mn_i , Mn_i - Mn_s pairs and Mn_s - Mn_i - Mn_s triplets. Our data show that regardless of the coordination, Mn_i always occupies T_{As} sites (top).

as a function of annealing temperature. We are currently carrying out such studies.

T_{As} occupancy is consistent with the expectation of having the Mn cations (substitutional as well as interstitial) coordinated by As anions rather than Ga cations. For Mn_i - Mn_s complexes, however, one could expect the Coulomb attraction between oppositely charged Mn_s acceptors and Mn_i donors to counteract the repulsion between positively charged Mn_i and Ga cations, making the T_{Ga} site energetically more favorable. More specifically, since the distance between neighboring S_{Ga} and T_{Ga} sites (2.45 Å) is smaller than that between neighboring S_{Ga} and T_{As} sites (2.83 Å), the decrease in Coulomb energy by decreasing the Mn_s - Mn_i distance (from T_{As} to T_{Ga}) could eventually counteract the increase in energy of changing the Mn_i coordination from As to Ga cations. However, our results show that even if this occurs, the gain in energy associated with having the Mn_i cations coordinated by As anions is still the dominant factor, irrespective of the Coulomb interaction in Mn_i - Mn_s

complexes.

In summary, we have shown that interstitial Mn occupies only T_{As} sites both before and after thermal annealing at 200°C, which implies that T_{As} is the energetically favorable site regardless of the interstitial Mn atom being isolated or forming complexes with substitutional Mn. These results solve the long standing controversy regarding T_{As} versus T_{Ga} occupancy, thus contributing to the understanding of electric and magnetic self-compensation in (Ga,Mn)As.

Acknowledgments

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4.6 Supplementary information

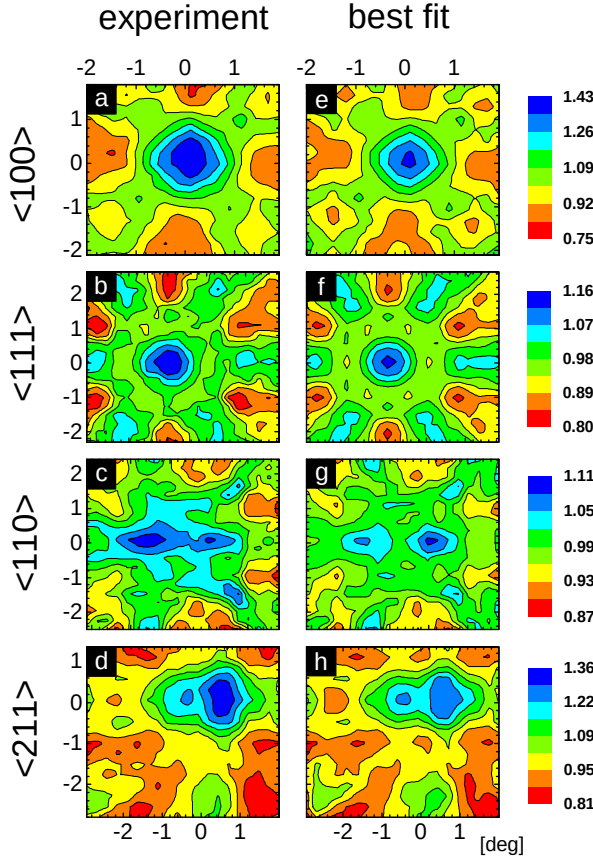


Figure 4.4: (a-d) Experimental β^- emission patterns of experiment C before thermal annealing, along the four measured directions, and best fits of theoretical patterns (e-h). The best fit is obtained for 79% of the ^{73}As atoms on S_{As} sites. The remaining 21% are located in low-symmetry sites, most likely in disordered regions created upon ^{73}As implantation.

In both experiments C and D, thermal annealing induces the recovery of damaged regions created upon implantation, leading to an increase in substitutional ^{73}As fraction. The same was observed for the substitutional ^{56}Mn fraction

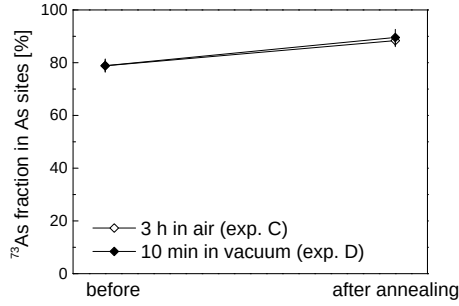


Figure 4.5: Fractions of ^{73}As atoms in S_{As} sites in experiments C and D.

(experiments A and B), which therefore can also be interpreted as due to lattice recovery, as mentioned in the main text.

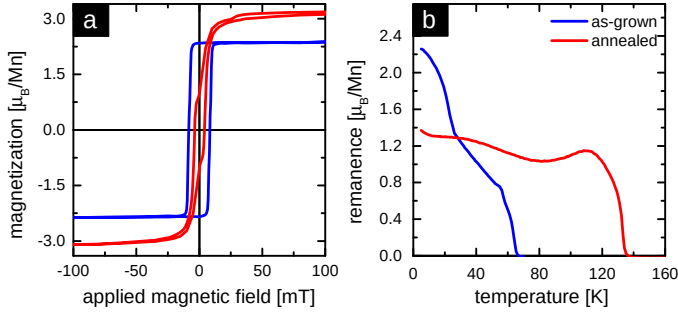


Figure 4.6: Magnetization data before (as-grown film) and after annealing for 3 h in air (experiment B): (left) magnetization as a function of applied magnetic field at 5 K; (right) magnetization as a function of temperature, with an applied field of 1 mT after field cooling under a saturating field of 100 mT.

Annealing for 3 h in air increases the saturation magnetization from 2.34 to 3.2 B/Mn and T_C from 67 to 137 K (Fig. 4.6). The saturation magnetization before/after annealing is consistent with an interstitial fraction of 20/10% (consistent with,^{29,60} i.e. a decrease by a factor of two, which is consistent with the decrease observed with emission channeling.

Chapter 5

Thermal stability of interstitial and substitutional Mn in ferromagnetic (Ga,Mn)As

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5.1 Abstract

In (Ga,Mn)As, a model dilute magnetic semiconductor, the electric and magnetic properties are strongly influenced by the lattice sites occupied by the Mn atoms. In particular, the highest Curie temperatures are achieved upon thermal annealing in a narrow temperature window around 200°C, by promoting the diffusion of interstitial Mn towards the surface. In this work, we determined the thermal stability of both interstitial and substitutional Mn in ferromagnetic (Ga,Mn)As thin films, using the emission channeling technique. At a higher Mn concentration, the temperatures at which substitutional and interstitial Mn become mobile not only decrease, but also become closer to each other. These findings advance our understanding of self-compensation in (Ga,Mn)As by showing that the strong dependence of the Curie temperature on annealing temperature around 200°C is a consequence of balance between diffusion of interstitial Mn and segregation of substitutional Mn.

5.2 Introduction

(Ga,Mn)As, a dilute magnetic semiconductor (DMS), is a model system for studying carrier-mediated ferromagnetism in semiconductors and the associated spintronic phenomena.^{5,39,199} In ferromagnetic (Ga,Mn)As thin films, which are typically grown by low-temperature molecular beam epitaxy (LT-MBE), Mn atoms mainly occupy Ga sites with a minority fraction occupying interstitial sites.^{29,51,92} Substitutional Mn atoms (Mn_s) provide both the localized magnetic moment and the itinerant holes that mediate the magnetic coupling. On the other hand, interstitial Mn atoms (Mn_i) have a doubly compensating effect: magnetic compensation since Mn_i couple antiferromagnetically with Mn_s ; electric compensation since Mn_i are double donors.²⁹ At a given Mn concentration, the substitutional-to-interstitial ratio strongly influences the hole concentration, the Fermi level, and the effective magnetization provided by non-compensated Mn_s moments.^{5,25,29,39,51,92,199}

Previous studies on (Ga,Mn)As have focused on a careful optimization of the

synthesis and post-growth treatments, aiming to improve two key properties: the Curie temperature (T_C) and the magnetization.^{25, 29, 51, 92, 100} In these studies at high Mn concentration (several percent), interstitial Mn was found to out-diffuse during thermal annealing in the 160°C-200°C temperature range.^{22, 25, 60, 100} The highest T_C in (Ga,Mn)As (188 K) has been achieved for a Mn concentration of $\sim 12\%$ after growth at low temperature ($T_G \sim 200^\circ\text{C}$), followed by thermal annealing in air at 160°C.^{25, 100} Understanding the diffusion of interstitial Mn (i.e. its thermal stability) is crucial, as it defines the lower limit for the optimum annealing temperature window. In particular, the binding energy of the interstitial Mn in complexes such as Mn_s - Mn_i pairs and Mn_s - Mn_i - Mn_s triplets,^{101, 102} which can be as high as 0.8 eV,^{60, 65} contributes to its thermal stability. Therefore, since the fraction of Mn atoms in Mn_s - Mn_i pairs is expected to increase with increasing Mn concentration, so would the thermal stability of *interstitial* Mn. However this dependence has not been studied so far. On the other hand, the diffusion and segregation of *substitutional* Mn also plays a central role on the magnetic properties of (Ga,Mn)As, as it defines the upper limit for optimum annealing. Experiments based on ion channeling showed that part of the substitutional Mn is converted to a non-substitutional (random) component at annealing temperatures as low as $\sim 280^\circ\text{C}$.⁹² Additionally, a detailed study of the dependence of T_C on annealing temperature revealed a decrease in T_C with increasing annealing temperature in the range 160-220°C, suggesting an onset of segregation of Mn_s .²² However, these temperatures are well below the well-understood regime of secondary phase formation ($>400^\circ\text{C}$).^{101, 102, 117, 122} Moreover, direct evidence for Mn_s segregation around 200°C is still lacking.

The diffusion of interstitial Mn and the segregation of substitutional Mn in (Ga,Mn)As remain poorly understood. In this paper, we address this gap in understanding by studying the thermal stability of Mn in ferromagnetic (Ga,Mn)As with a concentration of 1% and 5%. Using the emission channeling technique, we observe that, with increasing Mn concentration, the temperatures at which Mn_s and Mn_i become mobile not only decrease, but also become closer to each other. These results show that the narrow annealing temperature window in which the T_C and magnetization can be optimized in (Ga,Mn)As results from a thin balance between diffusion of Mn_i and segregation of Mn_s .

5.3 Experimental Details

The emission channeling technique makes use of charged particles emitted by a decaying radioactive isotope, usually β^- decay electrons or conversion electrons.¹⁸⁰ These particles are emitted isotropically during decay and are channeled along the screened Coulomb potential of atomic rows and planes. Along low-index crystal directions of single crystals or epilayers, this anisotropic scattering results in well-defined channeling or blocking effects. Because these effects strongly depend on the initial position of the emitted particles, they produce emission patterns which are characteristic of the lattice sites occupied by the probe atoms. Emission channeling experiments were performed by implanting a low concentration ($< 0.05\%$) of radioactive ^{56}Mn (half-life $t_{1/2} = 2.56$ h) or ^{73}As (half-life $t_{1/2} = 80$ d) into (Ga,Mn)As thin films. Angular-dependent emission patterns are recorded along various crystallographic axes using a position- and energy-sensitive detection system similar to that described in Ref. 184. The theoretical emission patterns for probes occupying a large variety of possible lattice sites are calculated using the *manybeam* formalism for electron channeling in single crystals.¹⁸⁰ Quantitative lattice location is provided by fitting the experimental patterns with theoretical ones using a two-dimensional fit procedure.¹⁹² Corrections for backscattered electrons that reach the detector were implemented by multiplying the fitted fractions with a correction factor, which is equivalent to subtracting an isotropic background from every pattern. This backscattered electron contribution is estimated based on Geant4 simulations of electron scattering,^{188,189} taking into account the elemental composition and geometry of the sample, sample holder and vacuum chamber. By probing the site occupancy of the radioactive probes as a function of annealing temperature we can investigate their thermal stability.

To this purpose a series of emission channeling experiments were performed on (Ga,Mn)As films, grown using low temperature molecular beam epitaxy, as described in Refs [59, 100]. The samples and experimental details are given in Table 5.1. The quoted Mn concentrations ($[\text{Mn}]$) are estimated values based on a series of calibration measurements,²⁰⁰ and correspond to a density of $2.2 \times 10^{20} \text{ cm}^{-3}$, where x is the quoted $[\text{Mn}]$. The results from sample A and B

sample	[Mn]	t [nm]	isotope	E [keV]	R_p [nm]	σ [nm]	x_p [cm ⁻³]	fluence [cm ⁻²]	θ [°]
A	1%	1500	⁵⁶ Mn	30	21	11	2.4×10^{18}	7×10^{12}	17
B	5%	200	⁵⁶ Mn	30	21	11	2.4×10^{18}	7×10^{12}	17
C	5%	200	⁷³ As	50	26	13	1.5×10^{19}	5×10^{13}	10

Table 5.1: Sample and implantation details. All implantations were performed at room temperature. The peak concentrations (x_p), projected ion range (R_p) and straggling (σ) were estimated using SRIM-2008 code.¹⁹¹ The sample thickness, implantation energy and angle are denoted, respectively, by t , E and θ .

can be directly compared regarding the thermal stability of ⁵⁶Mn in (Ga,Mn)As with two different concentrations. The ⁷³As experiment, on sample C, was performed to probe the stability of the lattice of (Ga,Mn)As with 5% Mn when annealing up to high temperatures ($\sim 600^\circ\text{C}$). All implantations were performed at room temperature and subsequent measurements were carried out in the as-implanted state and after thermal annealing in steps of 50°C (100°C for the ⁷³As experiment) starting at 100°C . Each annealing step was performed in high vacuum ($< 10^{-5}$ mbar) for 10 min. Angular-dependent emission patterns were recorded along four crystallographic axes ($\langle 100 \rangle$, $\langle 111 \rangle$, $\langle 110 \rangle$ and $\langle 211 \rangle$) at room temperature.

5.4 Results and Discussion

Emission channeling results are presented and discussed in two parts starting with the identification of which lattice sites Mn occupies in (Ga,Mn)As (section 5.4.1), followed by the analysis of Mn diffusion and thermal stability for both Mn concentrations (section 5.4.2). This analysis includes a model for the diffusion of both Mn_s and Mn_i , as well as a discussion of its implications on the understanding of Mn thermal stability in (Ga,Mn)As.

5.4.1 Identification of the occupied lattice sites

In (Ga,Mn)As the Mn dopants occupy mainly Ga-substitutional sites S_{Ga} . Fitting calculated S_{Ga} patterns to our experimental results gives by far the best agreement. By including in the fitting tetrahedral interstitial sites with As closest neighbors (T_{As}), the best fit was observed for the $S_{\text{Ga}}+T_{\text{As}}$ double occupancy patterns, with larger fractions of ^{56}Mn probes occupying the S_{Ga} sites and smaller fractions the T_{As} sites. This is consistent with previous emission channeling experiments showing that interstitial Mn occupies only the T_{As} site, with $< 0.5\%$ of Mn occupying T_{Ga} sites.¹⁷⁹

As an example of the good match between experiment and simulated patterns, Fig. 5.1 compares the normalized experimental β^- emission yields for the ^{56}Mn experiment on sample A, after an annealing step at a temperature of 350°C , along the four measured directions (a-d) with the best fits to theoretical patterns (e-h). Site fractions for the best fit, averaged over $\langle 110 \rangle$ and $\langle 211 \rangle$ directions, give 65% of the ^{56}Mn atoms in S_{Ga} sites and 14% in T_{As} sites. For the radioactive ^{73}As experiment in sample C, the probes were found to occupy exclusively substitutional S_{As} sites, with a site fraction of $\approx 100\%$. Further details are given in the supplementary information. For all experiments presented in Table 5.1, fractions of other possible interstitial sites are estimated to be below 5%, within the measuring uncertainty.

5.4.2 Thermal stability of interstitial and substitutional Mn

Associated with each site is its occupancy, i.e. the fraction incorporated in the respective site with respect to all the implanted ^{56}Mn (or ^{73}As). Site fractions associated with the stable isotopes incorporated during growth will most likely differ, since the kinetics of implantation is very different from that of doping during LT-MBE growth. Once the Mn atoms are at rest their behavior does not depend on their history or isotope, and although the absolute site fractions may differ, the diffusion behavior we investigate here is accurately reproduced by the ^{56}Mn probes. Performing this experiment after several annealing steps provides information on the thermal stability of the occupied lattice sites.

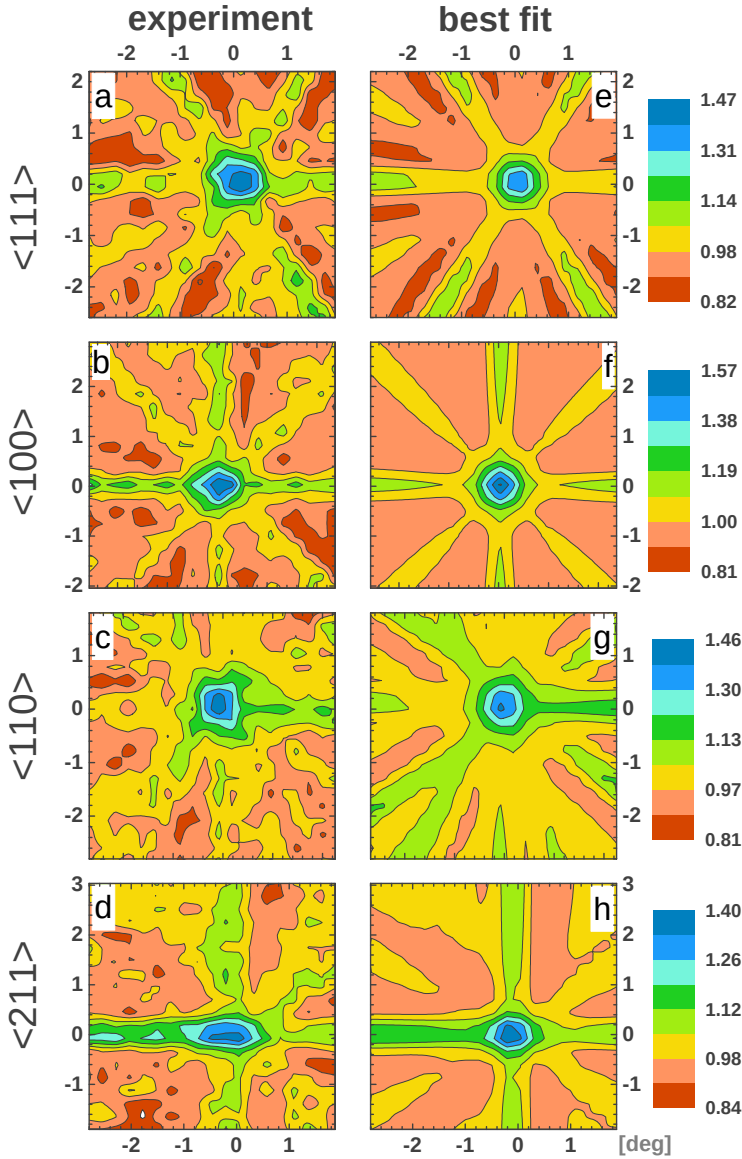


Figure 5.1: (a)-(d) Normalized experimental β^- emission channeling patterns in the vicinity of the $\langle 111 \rangle$, $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 211 \rangle$ directions of the (Ga,Mn)As film with 5% Mn, following annealing at 350°C. (e)-(h) Corresponding best fits. Fits averaged over $\langle 110 \rangle$ and $\langle 211 \rangle$ directions yield 65% and 14% of the Mn atoms on S_{Ga} and T_{As} sites, respectively.

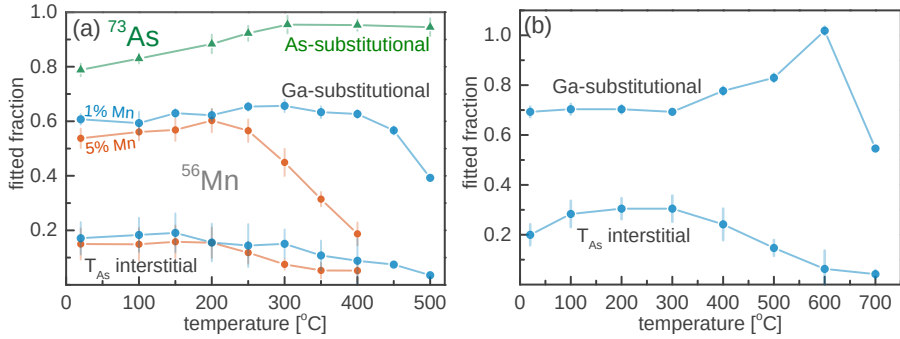


Figure 5.2: (a) Fitted fractions of implanted ^{73}As (green triangles) and ^{56}Mn (blue and orange circles) probes in (Ga,Mn)As samples doped with different concentrations of Mn, averaged over the $\langle 110 \rangle$ and $\langle 211 \rangle$ directions. (b) Fitted fractions of implanted ^{56}Mn probes in semi-insulating GaAs, extracted from Ref. 90.

Figure 5.2(a) shows the results from emission channeling experiments performed on samples A, B, and C, as a function of annealing temperature in comparison with the ultra-dilute case investigated in Ref. 90 (Fig. 5.2(b)). For each experiment the fitted fractions of ^{56}Mn or ^{73}As probes are plotted for the corresponding lattice sites they occupy, S_{Ga} and T_{As} for ^{56}Mn , and S_{As} for ^{73}As .

In emission channeling experiments, and in particular for (Ga,Mn)As thin films, two phenomena may induce changes in the obtained site fractions: (i) the annealing of implantation induced damage, and (ii) diffusion processes of the implanted probes. The first scenario (i) is observed in (Ga,Mn)As at relatively low annealing temperatures, and while the thermal energy is not sufficient to induce diffusion of Mn atoms, it induces crystalline recovery. In other words, during implantation many defects are created, such as Ga and As vacancies (V_{Ga} and V_{As}) and disordered regions, where radioactive ^{56}Mn probes may become trapped. Probes trapped in these regions emit electrons which will not be channeled due to the irregular potential surrounding them and will reach the detector with an isotropic distribution. On the other hand, radioactive probes can also combine with vacancies (V_{Ga} or V_{As}), contributing to an increase in substitutional site fractions. Annealing of implantation damage is visible in

Fig. 5.2(a), where substitutional fractions increase with increasing annealing temperatures up to 300°C, particularly noticeable in the ^{73}As experiment where the S_{As} fitted fraction increases to near 100%.

The second phenomenon (ii), the diffusion of implanted probes, may influence site fractions via two separate mechanisms. On the one hand, once radioactive probes become mobile and diffuse away from their initial position in the sample, this may lead to their incorporation in a different type of lattice site. This has been observed for instance for ^{56}Mn implanted into pure GaAs^{90,94} (cf. Fig. 5.2(b)), where the onset of the migration of interstitial $^{56}\text{Mn}_i$ in the temperature range 300-600°C leads to its incorporation in substitutional Ga sites as $^{56}\text{Mn}_s$ via the combination with Ga vacancies. On the other hand, diffusion also leads to changes in the depth profile of the implanted probes. In that respect, although diffusion occurs in every direction within the film, due to the nature of emission channeling only diffusion towards the surface or deeper into the sample will have an impact on the measured fractions. Electrons emitted from deeper within the sample (diffusion to the bulk) are subjected to stronger dechanneling effects, whereas electrons emitted from the first few atomic layers (diffusion towards the surface) do not experience channeling effects. In both cases electrons reach the detector as an isotropic contribution resulting in a decrease in the fitted fractions. We discuss this effect in more detail below, in the context of a Mn diffusion model.

Comparing the ^{56}Mn site fractions to our previous studies in pure GaAs, in Fig. 5.2(b), it is striking that no pronounced ^{56}Mn site changes from interstitial to substitutional sites are observed in (Ga,Mn)As. In GaAs, a decrease in interstitial ^{56}Mn fraction was accompanied by a corresponding increase in substitutional fraction. We attribute the absence of this effect to the fact that the (Ga,Mn)As samples are saturated with stable Mn_i , incorporated during growth, which fill essentially all Ga-vacancies created during implantation. Since the concentration of stable Mn_i is orders of magnitude larger than the implanted ^{56}Mn , only a negligible fraction of radioactive ^{56}Mn probes participate in this process, and therefore the site change is not observed. In addition, while in GaAs ^{56}Mn on substitutional Ga sites was completely stable against annealing up to a temperature of 600°C, in (Ga,Mn)As the substitutional fraction starts

to decrease at much lower temperatures. Moreover, there is a clear distinction between the experiments performed in samples A (1% Mn) and B (5% Mn), showing that the thermal stability of both substitutional and interstitial sites decreases with Mn concentration.

Ultimately, the difference in temperature at which the Mn on substitutional sites becomes mobile for both samples A and B, represented in Fig. 5.2, is related to a decrease in thermal stability with increasing Mn concentration. This points to a possible onset of Mn segregation at lower temperatures and as such sets an upper limit for the optimum annealing temperature at which T_C can be maximized in (Ga,Mn)As thin films.

The thermal stability of Mn in (Ga,Mn)As is further addressed in the following paragraphs, with an estimate of the activation energies for diffusion of both Mn_s and Mn_i from the emission channeling results presented above, within an adequate diffusion model.

5.4.2.1 Diffusion model

Activation energies for Mn diffusion in (Ga,Mn)As can be estimated from emission channeling data by fitting a modified Arrhenius model to the fractions shown in Fig. 5.2. The details of this calculation are given in the supplementary information (cf. section 5.6), and the model is described in the remainder of this section. The resulting activation energies for substitutional and interstitial diffusion are presented in Table 5.2 for both Mn concentrations in the (Ga,Mn)As under study. Additionally, activation energies for ^{56}Mn diffusion in GaAs from Ref. 90 are also included for comparison. The main observation from Table 5.2 is that the activation energies E_a^i and E_a^s decrease with increasing Mn concentration, i.e. for both substitutional and interstitial Mn. In this section, we discuss this observation in more detail and introduce a model for diffusion of Mn in (Ga,Mn)As.

In the ultra-dilute regime ($< 0.05\%$ Mn), where only the implanted ^{56}Mn probes contribute to the total Mn concentration in GaAs, Mn_i can be assumed to diffuse as a free, isolated interstitial.^{190,195} In other words, the probability

% Mn	substitutional		interstitial	
	$T_{1/2}$ [°C]	E_a^s [eV]	$T_{1/2}$ [°C]	E_a^i [eV]
0.05	700	2.9	450 – 550	1.7 – 2.3
1	500 – 550	2.4	350 – 450	1.6 – 2.0
5	350 – 400	1.9	250 – 300	1.3 – 1.6

Table 5.2: Estimated activation energies E_a for substitutional and interstitial Mn diffusion in (Ga,Mn)As with different Mn concentrations. $T_{1/2}$ represents the temperature range at which our fitted fractions reduce to $f_0/2$. $T_{1/2}$ is described in more detail in the supplementary information (section 5.6).

for a Mn_i atom to occupy a position near a Mn_s atom is very small, as Mn impurities are far apart in an ultra-dilute system. In this scenario the activation energy for free interstitial diffusion can then be directly related to the *migration energy* E_m , which is the energy barrier between neighboring interstitial sites. Since Mn_i was observed to only occupy T_{As} sites both before and after thermal annealing in ferromagnetic (Ga,Mn)As (cf. chapter 4),¹⁷⁹ E_m can be specifically attributed to the energy barrier between neighboring T_{As} interstitial sites. This scenario implies that T_{Ga} is a higher-energy configuration compared to T_{As} , so that the barrier associated with a $\text{T}_{\text{As}} \rightarrow \text{T}_{\text{Ga}}$ jump is larger than the reverse $\text{T}_{\text{Ga}} \rightarrow \text{T}_{\text{As}}$. This also implies that at room temperature the $\text{T}_{\text{Ga}} \rightarrow \text{T}_{\text{As}}$ barrier is overcome, resulting in the prevalence of T_{As} sites. Thus, we can conclude that interstitial diffusion occurs along the path $\text{T}_{\text{As}} \rightarrow \text{T}_{\text{Ga}} \rightarrow \text{T}_{\text{As}}$, depicted in Fig. 5.4, and its activation energy is directly linked with E_m , $E_a^i = E_m$.

In the higher concentration regime investigated in this paper, the interstitial diffusion can not be solely modeled by $E_a^i = E_m$, as a considerable fraction of the interstitials are trapped by neighboring substitutional Mn, forming pairs ($\text{Mn}_s\text{--Mn}_i$) and triplets ($\text{Mn}_s\text{--Mn}_i\text{--Mn}_s$) (cf. Fig. 5.4). These complexes contribute to the activation energy for interstitial diffusion with E_b^i , an additional energy barrier that Mn_i has to overcome to break the bond with substitutional Mn, resulting in $E_a^i = E_m + E_b^i$. Following a purely statistical approach, as described in Ref. 198, i.e. assuming that the substitutional Mn is randomly distributed in the lattice, the fractions of isolated substitutional Mn atoms (x_s) and of pairs of neighbouring substitutional Mn atoms ($x_{s\text{--}s}$) as a function of Mn concentration

x can be calculated by: $x_s = (1 - x)^{12}$ and $x_{s-s} = 12x(1 - x)^{18}$. For 1% Mn, this gives $x_s = 0.89$ and $x_{s-s} = 0.10$. For 5%, $x_s = 0.54$ and $x_{s-s} = 0.24$. In other words, the probability of interstitial Mn_i to be trapped by complexes involving more than one substitutional Mn_s is considerably enhanced for $[Mn] = 5\%$. E_b^i can then be described as an energy barrier that is largely determined by the Coulomb interaction between oppositely charged Mn_s and Mn_i defects, and should, intuitively, increase with the number of Mn_s atoms involved in the complex. Density functional theory (DFT) calculations have indeed predicted this effect, with binding energies of $E_b^{\text{pair}} = 0.49$ eV for the $Mn_i(T_{As})-Mn_s$ bond, and $E_b^{\text{triplet}} = 0.81$ eV for $Mn_s-Mn_i(T_{As})-Mn_s$ bonds.⁶⁵

Given the statistical prevalence of Mn complexes at higher concentrations, one would expect the activation energy for interstitial diffusion to increase with Mn content. However, the emission channeling results presented here show the contrary, i.e. the activation energy for diffusion of interstitial Mn decreases with Mn concentration (cf. Table 5.2), which clearly points towards an additional diffusion enhancing mechanism. We propose that, while increasing Mn concentration adds a binding contribution to the activation energy for interstitial diffusion, associated with the Coulomb interaction between a single Mn_s and a Mn_i atom, the same Coulomb interaction between the interstitial and more distant Mn_s defects decreases the activation energy by an amount Δ , thus enhancing diffusion. Within a percolation cluster of Mn_s atoms, the Coulomb interaction energy between Mn_s^- and Mn_i^{2+} at a distance of 10 Å in a 5% (Ga,Mn)As sample can be estimated as $\Delta \approx 0.2$ eV, taking the GaAs dielectric constant (13.2). However, within a distance of 10 Å in a 5% Mn sample there are six Mn_s in the neighborhood of each Mn_i , resulting in possible potential modifications of the order of $\Delta \approx 1.2$ eV. A similar estimation can be performed for a 1% sample, resulting in an interaction energy of the order of $\Delta \approx 0.8$ eV. These energies can effectively compete with E_b^i , ultimately driving down the activation energy for interstitial diffusion, $E_a = E_m + E_b - \Delta$.

Comparing values for E_a^i in Table 5.2 with E_b^i from Ref. 65, discussed above, suggests that the activation energy for interstitial diffusion E_a^i decreases from the ultra-dilute regime to 5% Mn by $\Delta E_a^i \sim 0.1 - 1.0$ eV, driven essentially by the competing contributions from E_b^i and Δ , assuming similar E_m . However,

E_m requires additional discussion. In the ultra-dilute regime E_a^i is entirely due to E_m ($E_a^i = E_m$), and E_a^i is in fact larger than the values determined here for 1% and 5%. Therefore, E_m may also decrease from the ultra-dilute to the few percent regime. A possible contribution to this decrease is the lattice expansion induced by the Mn doping, i.e. that interstitial Mn experiences a lower migration barrier in a more open lattice. However, the lattice expansion from the ultra-dilute case to 5% Mn in (Ga,Mn)As layers only results in an increase of 0.2% in lattice constant, according to Ref. 200. Nevertheless, even if this decrease is significant in E_m , it alone cannot explain all the observed changes in E_a^i ; in that case, E_a^s would vary by the same amount, which is not observed. In order to explain the additional variation, Δ is required.

The diffusion of substitutional Mn, on the other hand, can be assumed to be of the Frank-Turnbull type, i.e. thermally activated Mn_s first leaves its substitutional lattice site and then diffuses as an interstitial until it encounters the next stable trap, usually a Ga vacancy. At sufficiently high Mn concentrations, also regions with segregated Mn can act as traps. The activation energy for this type of diffusion can be split in two terms, one consisting of the binding energy $E_b(Mn_s)$ of Mn to the substitutional site, the other being the activation energy E_a^i for interstitial diffusion of Mn_i , resulting in a total activation energy of $E_a^s = E_a^i + E_b(Mn_s)$. Note that for this type of diffusion mechanism, an increase or a decrease of the activation energy for interstitial diffusion will also lead to a corresponding effect on the stability of the substitutional Mn species. As established above, Δ drives down the activation energy for interstitial diffusion, and consequently, also the energy for substitutional diffusion, in accordance with the results in Table 5.2.

A different model for the diffusion of Mn in (Ga,Mn)As has been proposed in Refs. [201, 202], which considers that clustering of Mn occurs via pure substitutional diffusion driven solely by Ga vacancies (V_{Ga}). The weakness of this model is that it neglects the interaction of Mn interstitials with Ga vacancies, i.e. the fact that interstitial Mn, once it becomes mobile, easily converts to substitutional by filling up existing V_{Ga} (which is associated with an energy gain). The reverse process, i.e. dissociation of Mn_s by becoming interstitial and leaving behind a V_{Ga} , is also possible, though only with higher thermal activation

energy, cf. the discussion above. In contrast, it is assumed in Refs. [201, 202] that Mn interstitials have been completely driven out from the sample before clustering of substitutional Mn atoms starts. Moreover, the substitutional diffusion of Mn is assumed to be the consequence of a rather high concentration of mobile V_{Ga} ($\approx 1 \times 10^{18} \text{ cm}^{-3}$), which is not explained by the model itself but given as external input. The assumption that interstitial out-diffusion of Mn in (Ga,Mn)As can be entirely completed before any substitutional diffusion starts is contrary to what we observe in our emission channeling experiments, especially in the 5% Mn sample, where the decrease in interstitial and substitutional Mn fractions takes place in overlapping temperature regimes, i.e. the two processes occur simultaneously, though slower for substitutional Mn.

5.4.2.2 Substitutional Mn diffusion as a limiting factor

The temperature at which substitutional Mn becomes mobile changes from 700°C in the ultra-dilute regime, to $\sim 500^\circ\text{C}$ at 1% [Mn], to $\sim 350^\circ\text{C}$ at 5% [Mn]. Although the formation of MnAs precipitates is well documented in the 400–600°C temperature range,^{101, 102, 117, 122} our data show that this segregation process can already take place at lower temperatures, likely with the formation of disordered Mn-rich regions preceding well-defined secondary phases. This scenario is further supported by the emission channeling data obtained upon re-implanting ^{56}Mn after high temperature annealing (400°C for 5% and 500°C for 1% Mn), i.e. after diffusion of a significant fraction of substitutional Mn. A thorough analysis of this effect is beyond the scope of this paper and is therefore only briefly described in the supplementary information (section 5.6).

At several % Mn, segregation may occur at annealing temperatures as low as 200°C, counteracting the improvement of T_C by removal of interstitials, introducing an upper limit for the optimum annealing temperature. On the other hand, the lower limit is determined by the removal of interstitial Mn. From our results (Table 5.2), the activation energy E_a^i for interstitial diffusion also decreases with Mn concentration, although less significantly than for substitutional. The annealing temperature window for T_C and magnetization optimization in (Ga,Mn)As is therefore narrowed and limited by two phenomena

which have opposite effects on T_C : interstitial out-diffusion and substitutional low-temperature segregation. Although these two processes are governed by rather close activation energies, it is possible to induce the diffusion of interstitial Mn (with a lower activation energy) while minimizing substitutional segregation, as long as the thermal annealing is sufficiently long and at a suitably low temperature (typically several hours for films ~ 25 nm at temperatures of 160–180°C).²² In this picture, film thickness also plays an important role. Decreasing the thickness also decreases the diffusion distance required for interstitial Mn to be passivated at the surface. In contrast, the segregation of substitutional Mn is in principle unaffected by a reduction in thickness since the required diffusion length is determined in that case by the (local) Mn concentration. Therefore, thinner films favor passivation of interstitial Mn and, indeed, the highest T_C and magnetization are observed in thinner films, typically ~ 25 nm.²²

5.5 Conclusion

This work addresses the lattice location and thermal stability of Mn in ferromagnetic (Ga,Mn)As doped with 1% and 5% Mn. The majority of Mn atoms have been found to substitute Ga sites, while a significant fraction occupies tetrahedral interstitial sites with As nearest neighbors.

The thermal stability of both substitutional and interstitial Mn decrease with Mn concentration, with estimated activation energies for diffusion of *interstitial Mn* at 1.6 – 2.0 eV for 1% and 1.3 – 1.6 eV for 5% Mn, and of *substitutional Mn* at 2.4 eV and 1.9 eV, respectively. This decrease in thermal stability at a few % Mn content is directly related to an increased Mn diffusivity in (Ga,Mn)As films, which we attribute to the Coulomb interactions between substitutional Mn and diffusing interstitial Mn atoms.

These findings shed new light on our understanding of Mn self-compensation in (Ga,Mn)As. The delicate balance between interstitial and substitutional thermal stability defines the narrow temperature window in which the Curie temperature and the magnetization can be maximized. The lower limit is defined by the mobility of Mn interstitials towards passivation at the surface, whereas the

higher limit is limited by the mobility of substitutional Mn, i.e. the onset of Mn segregation into secondary phases. Since the Mn concentration affects more strongly the upper limit, the optimal annealing temperature window narrows down with increasing Mn concentration.

Acknowledgments

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5.6 Supplementary Information

5.6.1 Re-implantation after segregation

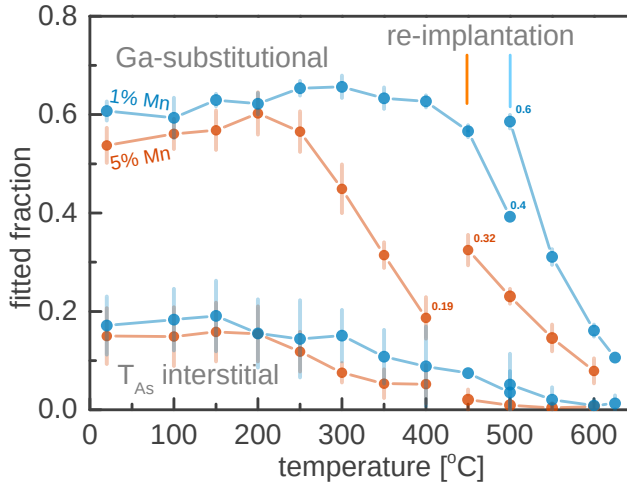


Figure 5.3: Complete data from experiments on samples A and B. Fitted fractions of implanted ^{56}Mn probes in $(\text{Ga},\text{Mn})\text{As}$ with different Mn concentrations. Data points beyond the indicated colored bars were taken after re-implantation of ^{56}Mn probes, in a regime where Mn_s has already started clustering, and the local Mn concentration has decreased, giving rise to discontinuities.

Annealing at temperatures above $T > 400^\circ\text{C}$ induces Mn segregation into superparamagnetic MnAs nano-sized clusters.^{117,122} Fig. 5.3 presents the full results of the emission channeling experiments detailed in the main text. Compared to Fig. 5.2, a few points are added for the experiments performed after re-implantation of ^{56}Mn probes, at annealing steps up to $T = 630^\circ\text{C}$. The discontinuities at 450°C and 500°C , for 5% Mn and 1%, respectively, correspond to measurements performed after re-implantation of ^{56}Mn at room temperature into the samples that had previously been annealed at 400°C and 500°C . Note that the re-implanted samples were then annealed as indicated in the figure before proceeding with the measurements. Since Mn_s was already mobile in the annealing steps prior to the re-implantation of ^{56}Mn , the local

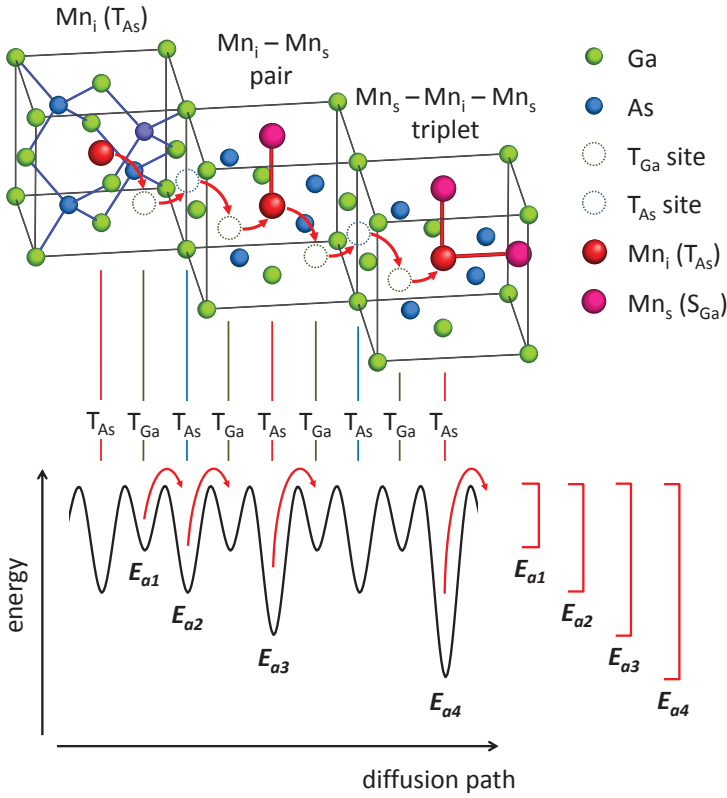


Figure 5.4: (Top) Interstitial Mn as a free interstitial, in a Mn_i-Mn_s pair and in a Mn_s-Mn_i-Mn_s triplet. The red arrows indicate successive T_{As} → T_{Ga} → T_{As} diffusion steps between the three configurations. (Bottom) Energy landscape across the same diffusion path, depicting the activation energies used in the model described in the text. This model only describes the effect of E_m and E_b on the diffusion, i.e. the Δ contributions described in the main document are not represented. In this model, E_{a2} is the same as E_m .

Mn concentration has decreased with Mn_s segregation, effectively changing Mn diffusivity. Accordingly, the freshly implanted probes experienced a higher thermal stability, which ultimately led to an increase in fitted fractions.

5.6.2 Interstitial Mn diffusion model

Within an Arrhenius model of thermally activated migration, similar to the one described in Refs. [90,94], the fraction $f(T, \Delta t)$ of Mn on a T_{As} interstitial site after an annealing step of duration Δt at a temperature T is given by:

$$f(T, \Delta t) = f_0 \exp[-\nu_0 \Delta t / N \exp(-E_a / k_B T)] \quad (5.1)$$

where f_0 is the initial interstitial fraction before annealing, ν_0 is the attempt frequency, which we take as 10^{12} s^{-1} , i.e. of the order of lattice vibrations, k_B is the Boltzmann constant, and N is the average number of jumps a Mn_i takes before it becomes immobilized in a cluster, at the substrate or at the surface. By taking the temperature range T_D in which the initial fraction reduces to half ($f(T_D) = f_0/2$), conservative limits for the activation energy E_a can be estimated.

If the diffusing Mn is considered to be a free interstitial, N includes every $T_{As} \rightarrow T_{Ga} \rightarrow T_{As}$ jump along the diffusion path. In the percent Mn regime investigated here, this assumption does not apply as a significant fraction of the interstitial impurities would be in Mn_s - Mn_i or Mn_s - Mn_i - Mn_s configurations. Fig. 5.4 demonstrates such a diffusion process detailing the required activation energies for each type of jump, E_{a1} , E_{a2} , E_{a3} and E_{a4} . Accordingly, N can be approximated as the number of jumps between trapping Mn_s centers, safely neglecting the jumps between adjacent interstitial sites, since E_{a3} and E_{a4} are a few tens of eV (E_b) higher than E_{a2} .⁶⁵ In other words, once the temperature is high enough to overcome E_{a3} and E_{a4} , the jump frequency associated with E_{a2} becomes so large that the time between E_{a3} or E_{a4} jumps is larger than that of the successive E_{a2} jumps required for Mn_i to travel between two neighboring Mn_s centers.

Statistically, in a 3-dimensional random walk, the root mean square (rms) distance from the origin after N jumps is given by $\sigma_{3,i} = \langle r^2 \rangle^{1/2} = \sqrt{N} d_i$, where d_i is the average distance between the complexes (which can be inferred from $x(1Mn_s)$ and $x(2Mn_s)$, introduced in the main document). Within the "thin-film" approximation, the impurity distribution is uniform along two of the

three directions, and therefore only jumps in the last direction will contribute to an observable diffusivity, i.e. one third of the jumps $N/3$. This expression then reduces to $\sigma_{1,i} = \sqrt{\frac{N}{3}} d_i$. In an emission channeling experiment the implanted impurities describe a nearly Gaussian depth distribution centered at the projected range R_p . Based on the channeling/dechanneling arguments outlined in the main document, $\sigma_{1,i}$ can be approximated to the projected range of implantation R_p , resulting in $N \approx 3 \left(\frac{R_p}{d_i} \right)^2$. Since the average distance d_i depends on the trapping center ($\text{Mn}_s\text{-Mn}_i$ or $\text{Mn}_s\text{-Mn}_i\text{-Mn}_s$), different E_a values are obtained for either E_{a3} -limited or E_{a4} -limited diffusion. This estimation resulted in the following values for N : for sample A (1% Mn), $N_{E_{a4}} \approx 100$ and $N_{E_{a3}} \approx 450$, and for sample B (5% Mn), $N_{E_{a4}} \approx 500$ and $N_{E_{a3}} \approx 1300$. Since the trapping mechanism by these two predominant types of Mn complexes act simultaneously, a realistic estimate of E_a is given by the range between lowest minimum and highest maximum of the two cases, corresponding to the E_a values present in Table 5.2 from the main document.

Chapter 6

Manganese segregation in (Ga,Mn)As

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6.1 Abstract

Hybrid structures with ferromagnetic MnAs nanoclusters are a promising alternative to dilute magnetic semiconductors in the field of spintronics. The formation of secondary-phases in (Ga,Mn)As films by annealing above 500°C is widely understood, and is characterized by the formation of ferromagnetic MnAs zincblende and/or NiAs-type nanoclusters. Here we present structural and magnetic studies on (Ga,Mn)As annealed at various temperatures, resulting in three phases: ferromagnetic (Ga,Mn)As with high T_C , disordered paramagnetic Mn-rich nanoclusters in GaAs:Mn, and superparamagnetic MnAs nanoclusters in GaAs:Mn. In particular, we present a detailed characterization of the disordered phase formed after annealing at 300°C.

6.2 Introduction

Dilute magnetic semiconductors (DMS) display an intricate interplay between structural and magnetic properties.^{5,199} Going beyond standard semiconductor technology by combining semiconducting and magnetic properties enables further functionalities, such as non-volatility, higher speed and lower power consumption, as well as the possible integration into new multi-functional devices in quantum electronics.^{13–15} (Ga,Mn)As is the model dilute magnetic semiconductor, typically grown by low-temperature molecular beam epitaxy (LT-MBE),⁵⁹ and ferromagnetic with Curie temperatures T_C up to ~ 200 K after thermal treatment.²⁵ Room-temperature ferromagnetism has been predicted in this compound for Mn concentrations above 5% and hole concentrations of 10^{20} cm^{-3} ,²⁸ but it has not yet been achieved due to the incorporation of Mn into interstitial positions. Interstitial Mn defects act as double donors, effectively reducing hole concentrations and coupling antiferromagnetically with ferromagnetic substitutional Mn moments,²⁰³ limiting a high Curie temperature and magnetization. Thermal annealing close to growth temperature is currently the most efficient method to partially remove interstitial Mn defects. The highest achieved Curie-temperature using this method holds its record at 185 K for a

concentration of 10% Mn, after thermal annealing in air at 160°C.²⁵ Annealing at slightly higher temperatures, however, results in lower Curie-temperatures,²² indicating that careful and well controlled low-temperature annealing is required in order to promote out-diffusion of Mn interstitial defects and effectively increase T_C in (Ga,Mn)As.^{60,92} Annealing at higher temperatures, above 500°C, resulted in higher T_C values, related to the formation of superparamagnetic secondary phases within the alloy and not representative of dilute magnetism.

(Ga,Mn)As films annealed at temperatures above 500°C typically exhibit spinodal decomposition into granular hybrid structures consisting of ferromagnetic MnAs nanoclusters embedded in a paramagnetic GaAs:Mn matrix.^{13,105–108,204} The formation of this hybrid phase with embedded MnAs nanoclusters is also a promising alternative to the field of spintronics, as the nanoclusters can show ferromagnetic behavior even at room temperature.^{13,39,109} Stacked into heterostructures with semiconductors and/or metallic layers, this hybrid phase creates interesting phenomena such as a large tunneling magnetoresistance ratio observable at room temperature,^{110,111} or giant magnetoresistance effects in layered structures.^{112,113} These effects can be modulated by the structural and magnetic properties of the MnAs nanoclusters embedded in the GaAs:Mn layer, and can be tuned in a wide range by adjusting, e.g. cluster size, shape and/or distribution in the host material.¹⁰⁸

Extensive research has been dedicated over the past decade on tuning the structural and magnetic properties of MnAs nanoclusters embedded in GaAs:Mn layers. Two distinct types of MnAs nanoclusters have been observed in annealed (Ga,Mn)As layers with different crystallographic structures: cubic *zincblende* and hexagonal *NiAs-type*. Annealing (Ga,Mn)As layers with low Mn content ($x \leq 5\%$) at relatively low temperatures, $T_A \leq 500^\circ\text{C}$, leads to MnAs segregation into small zincblende nanoclusters with diameters between 2 and 10 nm.^{101,116,121} These nanoparticles grow maximally strained with the surrounding zincblende GaAs lattice,^{101,124} and are ferromagnetic above room temperature, with $T_C \sim 350\text{ K}$. On the other hand, annealing at higher temperatures, $T_A \geq 600^\circ\text{C}$, results in the formation of hexagonal NiAs-type nanoclusters.^{101,117,121} These clusters are typically larger than zincblende MnAs nanoclusters, with sizes easily reaching 20 nm, and are also ferromagnetic above room-temperature, with Curie-

temperatures between 330 and 370 K.^{116,119,127} Both types of MnAs clusters embedded in a GaAs:Mn matrix display ferromagnetic Curie temperatures larger than bulk MnAs crystals or thin films in a hexagonal NiAs-type structure, with a typical T_C of around 320 K.¹²⁸ Most research to date has focused on these clear tendencies, yet it remains challenging to predict which kind of nanoclusters is formed based only on the annealing conditions and Mn content of the layer.

In contrast, little attention has been given to the structural and magnetic properties of (Ga,Mn)As layers annealed at lower temperatures, between 200°C and 500°C. Ion-channeling experiments indicated onset of early Mn segregation in (Ga,Mn)As annealed at 282°C.⁹² Additionally, as described in chapter 5, we observed that the thermal stability of substitutional Mn atoms greatly decreases for annealing temperatures in this regime. This can, on the one hand, also be correlated with an early onset of MnAs segregation at low annealing temperatures, and, on the other hand, with the decreasing maximum T_C with increasing annealing temperature observed in dilute (Ga,Mn)As layers.²²

This study investigates the structure and magnetism of (Ga,Mn)As under various annealing conditions, with particular emphasis on the less-understood annealing regime at intermediate temperature (300°C). We observe three different structural and magnetic phases: (i) ferromagnetic and crystalline, with removal of interstitial Mn and consequential T_C increase (thermal annealing at 200°C); (ii) disordered paramagnetic Mn-rich inclusions in GaAs:Mn (300°C); and (iii) well defined zincblende and NiAs-type MnAs superparamagnetic secondary-phases (600°C).

6.3 Methodology

The different structural and magnetic phases were investigated in (Ga,Mn)As films with two different concentrations, 1% and 5%, and annealed at different temperatures. Structural characterization was performed using synchrotron x-ray diffraction (SR-XRD), extended x-ray absorption fine structure (EXAFS), and transmission electron microscopy (TEM), while magnetic characterization consisted of superconducting quantum interference

device (SQUID) magnetometry. The different experimental conditions and methods are described in the following sections.

6.3.1 Sample preparation

The samples consisted of a total of eight (Ga,Mn)As films, four per concentration, 1% and 5% Mn, grown by low-temperature molecular beam epitaxy in Nottingham University.⁵⁹ (Ga,Mn)As samples doped with 1% Mn were grown with a thickness of 1.5 μm on GaAs substrates, while 5% (Ga,Mn)As samples were grown with a thickness of 200 nm on AlAs buffer layers (100 nm), on GaAs substrates. For each concentration four samples were prepared with different annealing conditions: one sample was kept in the as-grown state, a second and a third sample were annealed at 200°C and 300°C, respectively, in air for 100 hours; and a last sample was annealed at 600°C in vacuum for 10 minutes.

6.3.2 Synchrotron radiation x-ray diffraction

Synchrotron radiation x-ray diffraction (SR-XRD) measurements were performed at the BM20B-Rossendorf beamline at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The XRD measurements utilized an incident photon energy of 11.5 keV, corresponding to a wavelength of $\lambda = 1.0789 \text{ \AA}$, and were performed in conventional high-resolution symmetrical $\theta - 2\theta$ (HR-XRD) and grazing incidence (GI-XRD) configurations. HR-XRD measurements scanned in the range of the (002) GaAs substrate peak, from 20.5° to 22.5°. The latter GI-XRD measurements were performed asymmetrically under an incidence angle of 1.5°. All measurements were recorded using a linear 1D Mythen detector with 1280 channels, measurement resolution of 0.01°.

6.3.3 Extended x-ray absorption fine structure

Fluorescence extended x-ray absorption fine structure (EXAFS) experiments were performed at the x-ray absorption spectroscopy station of the Dutch-Belgian Beamline (DUBBLE, BM26) at ESRF. The measurements were carried

out at the Mn K edge (6.5 keV) at 300 K. Background subtraction, data processing, and fitting made use of ATHENA and ARTEMIS from the IFEFFIT 1.2.11c package.^{205,206} Ab initio calculations (feff8)²⁰⁷ were used to determine the backscattering amplitude and phase shifts of the single scattering paths.

6.3.4 Transmission electron microscopy

The (Ga,Mn)As sample annealed at 300°C in air was prepared for transmission electron microscopy (TEM) cross section observation using conventional dimple and ion milling in order to achieve final electron transparency. The TEM micrographs were acquired using a Jeol 2100F operating at 200 kV and the lattice images were recorded by aligning with the [011] zone axis of the GaAs substrate.

6.3.5 SQUID magnetometry

The magnetic characterization was performed using a superconducting quantum interference device (SQUID) magnetometer (LOT-Quantum Design SQUID-VSM MPMS3), following strict procedures in order to avoid measurement artefacts and external magnetic contributions. These procedures were developed based on statistically relevant tests, which allowed us to determine the practical limits of SQUID magnetometry for the detection of ferromagnetism under various sample preparation, processing, and handling conditions.^{190,208} All measurements were carried out with in-plane applied magnetic field along the [110] axis.

6.4 Results

The crystal structure of both phases was investigated using SR-XRD measurements under two different geometries, high-resolution conventional Bragg-Brentano (HR-XRD) and asymmetric grazing incidence (GI-XRD). While the first geometry was useful in the identification of the different phases of

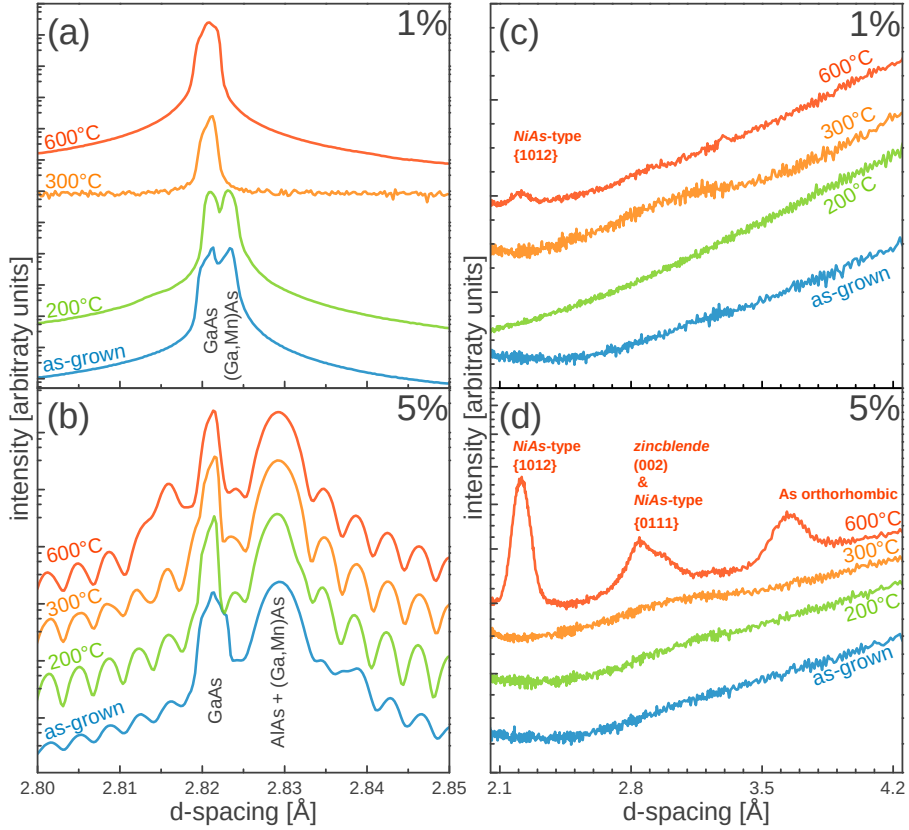


Figure 6.1: Synchrotron radiation x-ray diffraction (SR-XRD) measurements at room temperature with a wavelength of 1.0789 Å. (a)-(b) High-resolution symmetric $\theta - 2\theta$ scans around (002) GaAs substrate diffraction peak; (c)-(d) GI-XRD asymmetric scans performed at an incidence angle of 1.5°. No signature of non-coherent nanoclusters are observed for (Ga,Mn)As annealed at 300°C.

(Ga,Mn)As films, dilute versus hybrid, the second geometry allowed for a more thorough investigation of the secondary phases formed at higher annealing temperature (600°C). Figs. 6.1(a)-(b) show symmetric $\theta - 2\theta$ scans around the (002) GaAs diffraction peak as a function of annealing temperature for 1% and 5% (Ga,Mn)As, respectively.

Because (Ga,Mn)As films are strained on GaAs(100) substrates in the dilute phase,^{59,200,209} a buffer layer is required for the growth of thicker films at higher Mn concentrations. Such is illustrated in Figs. 6.1(a)-(b) by the separation between substrate and film peaks for both Mn contents. Moreover, the interference features observed on the wings of the substrate and film peaks in Fig. 6.1(b) result from the interference of the high luminosity x-rays reflected from the buffer and (Ga,Mn)As layers, which have nearly matching lattice constants, and demonstrate the high crystalline quality of these layers. On the other hand, we also observe a structural difference between measurements in the dilute and hybrid phases. Particularly for the 1% Mn samples, there is a relaxation of the film for annealing temperatures above 300°C, with the film peak converging to the GaAs substrate. At these temperatures Mn atoms segregate and form secondary phases embedded in a GaAs:Mn lattice, with an almost matching lattice constant to the substrate. This effect is not observed in the 5% Mn samples as it is not possible to independently determine the film's x-ray diffraction peak from the buffer layer's.

Since the secondary phases formed in hybrid phase probably consist of small MnAs nanoclusters embedded in a GaAs:Mn matrix, HR-XRD measurements are not able to distinguish their crystallographic structures due to the high intensity of substrate and (Ga,Mn)As diffraction peaks. Utilizing the second geometry indicated above, grazing incidence GI-XRD measurements are more sensitive to the (Ga,Mn)As layers than the substrate, probing only the first hundreds of nanometers from the surface. Accordingly, Figs. 6.1(c)-(d) plot the GI-XRD results, emphasizing secondary phases observed in each sample.

The presence of MnAs crystallites is clearly evident in samples annealed at the higher temperature, 600°C. In particular, x-ray diffraction peaks correspondent to both types of MnAs nanoclusters, zincblende and NiAs-type, were observed at a 5% Mn concentration, while for 1% only a small signature of zincblende

MnAs nanoclusters was observed. Additionally, there is also a contribution from As clusters, which is in accordance with observations in Refs. [122, 123]. In contrast, x-ray diffraction peaks are not visible for MnAs secondary phases in samples annealed at 300°C. This indicates that either the nanoclusters are too small for detection with GI-XRD, or that Mn segregation has not coalesced into well-defined crystalline phases, i.e. spinodal decomposition into disordered Mn-regions. This crystalline disorder was investigated using extended x-ray absorption fine structure (EXAFS), by probing the local neighborhood of Mn atoms in the various samples.

Figures 6.2(a)-(d) show EXAFS measurements on both Mn concentrations as a function of annealing temperature. The oscillations shown in Figs. 6.2(a)-(b) show the modulus of the Fourier-transformed $\chi(R)$ functions, from which the Mn-As nearest neighbor (NN) distance and the EXAFS Debye-Waller (DW) exponent can be calculated. In these figures there is a clear difference in $\chi(R)$ between dilute and hybrid samples, which can be attributed to the different local structure surrounding Mn atoms in each phase. In a dilute phase, Mn atoms are surrounded by As NN in a zincblende crystal lattice. This results in a shorter Mn-As bond than in the hybrid phase, in which Mn atoms have different local environments depending on the crystallographic structure of the nanocluster they reside in. This is further illustrated in Figs. 6.2(c) and (d), where the Mn-As NN distance and the EXAFS DW exponent are plotted.

We observe that, for the dilute samples, the Mn-As NN distance is consistent with the Ga-As distance in a GaAs lattice (2.45 Å), while for the hybrid GaAs:MnAs samples annealed at 600°C it is also in good agreement with the Mn-As NN distance in α -MnAs (2.57 Å),^{124, 210, 211} considering MnAs nanoclusters are strained within the GaAs:Mn matrix. The EXAFS DW exponent (Fig. 6.2(d)) is related to the disorder in the local structure of Mn atoms. Here, there is also a considerable difference between dilute and hybrid phases, a consequence of the ordering of the former and the segregation in the latter.

Interestingly, the samples annealed at 300°C differ slightly from the two previous cases, for while pertaining a comparable Mn-As NN distance to the dilute phase, they display a large EXAFS DW exponent, comparable to the hybrid phase. This suggests that this phase is locally equivalent to the dilute phase, although

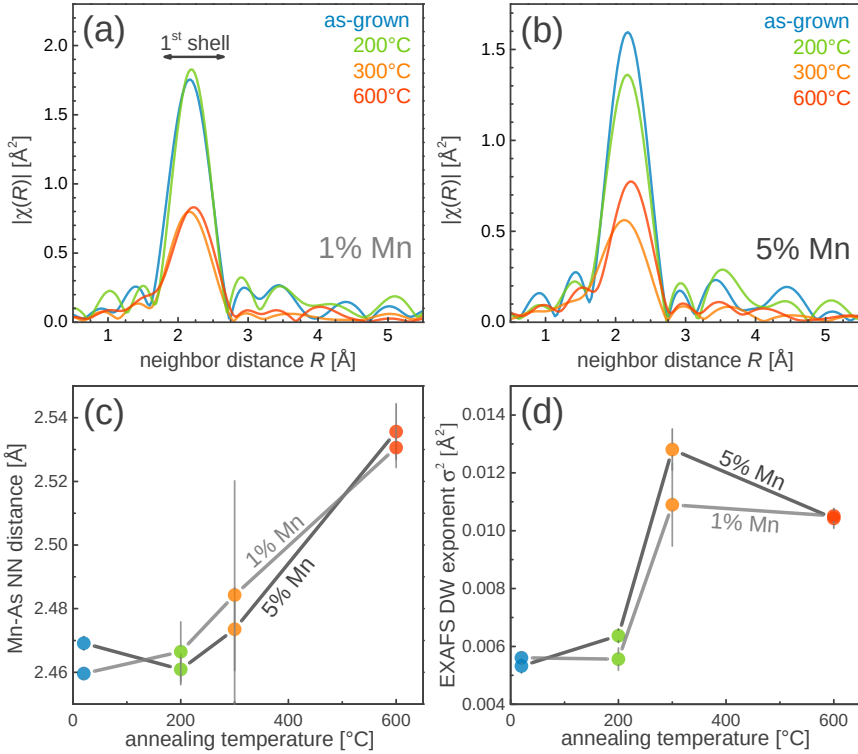


Figure 6.2: Extended x-ray absorption fine structure (EXAFS) data measured in the vicinity of the Mn K edge, at room temperature, as a function of annealing steps on (Ga,Mn)As. (a)-(b) Modulus of the Fourier-transformed $\chi(R)$ functions of EXAFS oscillations; (c) Distance to the nearest neighbors (NN) of the Mn atoms; (d) EXAFS Debye-Waller exponent for the first single scattering path of Mn absorbers in (Ga,Mn)As.

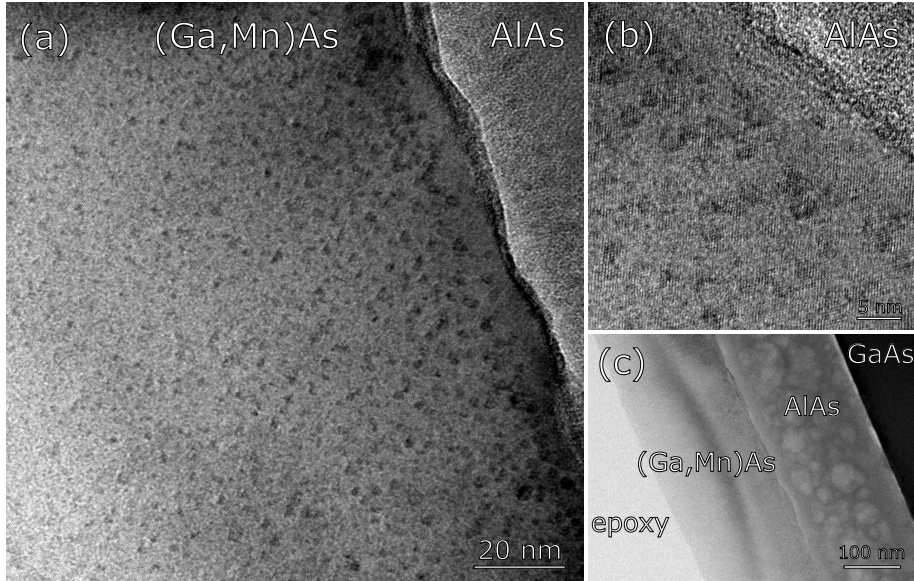


Figure 6.3: Transmission electron microscopy (TEM) micrographs taken from a 5% (Ga,Mn)As sample annealed at 300°C in air for 100 hours. (a) high magnification TEM micrograph near the interface between the (Ga,Mn)As film and with the AlAs buffer layer; (b) High resolution TEM (HR-TEM) of the darker features interpreted as due to disordered MnAs nanoparticles; (c) low magnification TEM micrograph showing the sample profile.

more disordered.

Evidence of Mn segregation at this annealing temperature is provided by transmission electron microscopy (TEM) measurements, performed on the 5% (Ga,Mn)As film annealed at 300°C, and is presented in Figs. 6.3(a)-(c). The presence of nanoclusters is visible in Figs. 6.3(a)-(b), with an average size ranging from 2 nm to 5 nm. While their composition cannot be extracted from TEM data, these nanoclusters are most likely Mn-rich, a consequence of Mn segregation during the annealing treatment at 300°C. Additionally, based on the SR-XRD and EXAFS results presented above, the observed nanoclusters are not crystalline, but highly disordered.

There is a clear structural difference between dilute and hybrid samples: while in the former Mn is randomly distributed in a highly crystalline lattice, in the

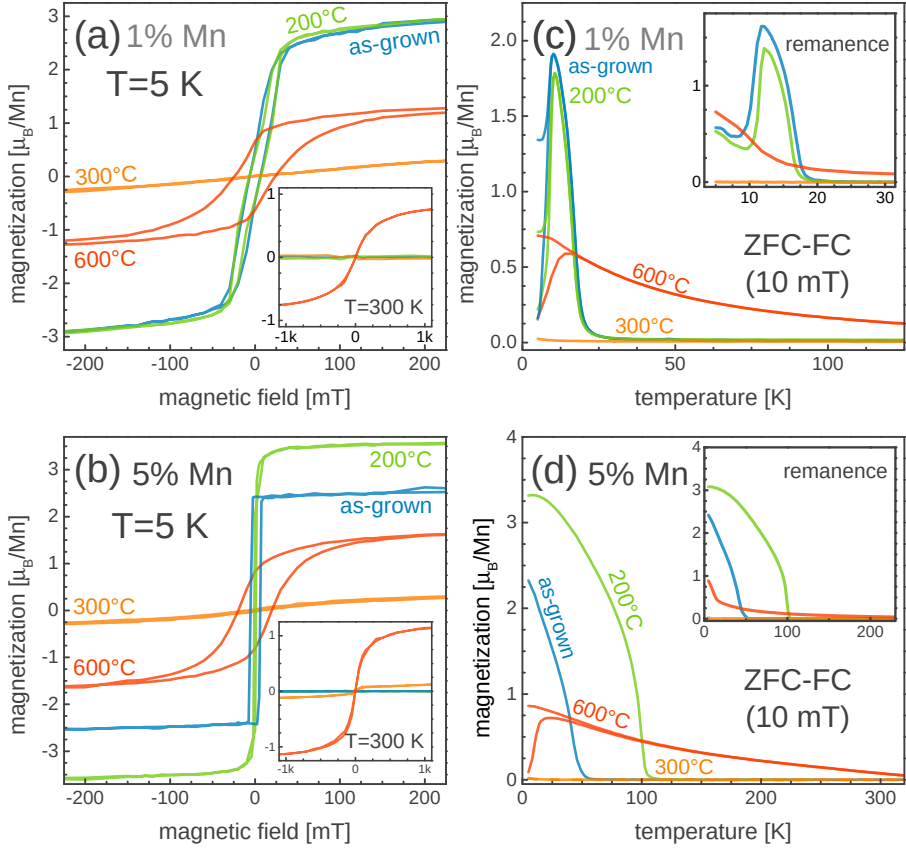


Figure 6.4: SQUID magnetometry measurements on (Ga,Mn)As as a function of Mn concentration for different annealing treatments: as-grown, and annealed at 200°C (100 h), 300°C (100 h) and 600°C (10 min); (a)-(b) magnetization as a function of applied magnetic field at 5 K and at 300 K (insets); (c)-(d) magnetization as a function of temperature, zero-field cooled (ZFC) and field-cooled (FC) at a magnetic field of 100 Oe, and at remanence magnetization (insets).

latter Mn atoms precipitate and form secondary-phases. These samples also show a wide range of magnetic states, which were investigated using **SQUID** magnetometry measurements (Figs. 6.4(a)-(d)).

The samples in the dilute state, i.e as-grown and annealed at 200°C, exhibit high magnetization and varying T_C , in good agreement with what is known for (Ga,Mn)As. Annealing around 200°C typically leads to an increase in magnetization and T_C in metallic (Ga,Mn)As layers, due to the removal of compensating interstitial Mn impurities. This is only observed for the 5% Mn samples (Fig. 6.4), where magnetization increases from $\approx 2.5 \mu_B/\text{Mn}$ to $\approx 3.5 \mu_B/\text{Mn}$ (cf. Fig. 6.4(b)), and T_C from ~ 50 K to ~ 100 K (cf. Fig. 6.4(d)). In the 1% Mn samples, however, this improvement was not observed as it is well known that interstitial Mn is not formed during **LT-MBE** growth of dilute (Ga,Mn)As layers at these lower concentrations.

Annealing (Ga,Mn)As layers at higher temperatures results not only in structural, but also magnetic changes in the system (Figs. 6.4). In particular, we observe different behaviors depending on the annealing treatment: while samples annealed at 300°C exhibit no ferromagnetic behavior, for samples annealed at 600°C there are clear signatures of superparamagnetism: magnetization versus magnetic field ((a) and (b)) following Langevin behavior and zero-field cooled (ZFC) and field-cooled (FC) irreversibility with blocking temperatures of $T_B(1\%) \approx 17$ K and $T_B(5\%) \approx 25$ K ((c) and (d)). The T_C for this superparamagnetic phase is above to 300 K, which is in good agreement with the presence of ferromagnetic MnAs nanoclusters embedded in a GaAs:Mn matrix. On the other hand, samples annealed at 300°C exhibit purely paramagnetic behavior. Although our data indicates Mn segregation (i.e. increased local concentration) which would generally lead to stronger magnetic interactions, the disorder observed with **EXAFS** is likely to have the opposite effect, resulting in paramagnetic behavior down to 5 K.

6.5 Discussion and conclusion

Thermal annealing has become the standard approach not only for achieving high T_C in (Ga,Mn)As films (typical annealing temperatures around 200°C), thanks to the out-diffusion of interstitial Mn defects, but also for creating hybrid GaAs:MnAs layers (typically around 500°C and higher temperatures), embedded with well-defined MnAs nanoclusters. Here, in addition to confirming these two regimes, we identified a new, intermediate state (upon annealing at 300°C) in which Mn-rich nanoclusters are formed, which are disordered and paramagnetic. Annealing at lower temperatures ($T \sim 200^\circ\text{C}$) promoted the well-known passivation of interstitial Mn, thus increasing T_C and the magnetization: for 5% Mn, T_C increased from ~ 50 K to ~ 100 K, and the magnetization from $\approx 2.5 \mu_B/\text{Mn}$ to $\approx 3.5 \mu_B/\text{Mn}$; for 1% no significant change was observed, since interstitial Mn is typically not formed during LT-MBE growth at such low Mn concentrations. At higher annealing temperature (600°C), as expected, well-defined ferromagnetic MnAs nanoclusters were identified, with both zincblende and NiAs-type structures. These clusters exhibit superparamagnetic behavior, with blocking temperatures $T_B(1\%) \approx 17$ K and $T_B(5\%) \approx 25$ K.

Further investigation of the intermediate regime reported here may provide insight on mechanisms to minimize Mn segregation in ferromagnetic layers, possibly yielding a path towards higher Curie temperature for this model dilute magnetic semiconductor. On the other hand, it may also open new pathways for the controlled formation of secondary phases in hybrid GaAs:MnAs layers, allowing for the tuning between zincblende or NiAs-type MnAs nanoclusters.

Acknowledgments

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Chapter 7

Manganese thermal stability in Ga-Mn-V ferromagnetic semiconductors

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7.1 Abstract

The exploration of different III-V hosts in dilute ferromagnetic semiconductors has been a cornerstone in the search for high-temperature ferromagnetic semiconductors in spintronic applications. Here we examine the local structure and thermal stability of Mn dopants, using the emission channeling technique, in Mn-doped dilute ferromagnetic semiconductors as the host is changed from GaP to GaAs to GaSb. A decreasing Mn thermal stability has been observed both in undoped semiconductors as well as in Mn pre-doped thin films. This decrease stems from the changing atomic packing between systems as well as from the charged nature of substitutional and interstitial Mn.

7.2 Introduction

Dilute magnetic semiconductors (DMS) have become the staple playground for investigating the interplay between structure and magnetism at the nanoscale over the past couple of decades.^{5,212} Harnessing the additional spin degree of freedom of the electron, DMS have demonstrated a variety of spintronic properties, such as spin injection and magnetism control through electric fields.^{213–215} Additionally, DMS display a large degree of tunability, in Curie temperature, magnetic anisotropy, band gap or carrier concentration, which creates an incredible potential for devising novel spintronic devices.^{5,16,29,39,199,216}

Mn-doped III-V semiconductors are considered model systems in which to investigate carrier-mediated ferromagnetism. From Mn-doped GaP to GaAs to GaSb, various ferromagnetic models aim to describe their properties, analysing localization trends, valence band versus impurity band, exchange interaction strengths and self-compensation.^{49,204,217–219} (Ga,Mn)As has been demonstrated to be the most successful DMS up to date, displaying both a high T_C and magnetization, which increase monotonically with Mn concentration and hole concentration.^{40,47,52,220} More specifically, T_C increases with *effective* Mn concentration, taking into account the balance between substitutional

and interstitial Mn fractions. Substitutional Mn atoms (Mn_s) provide both the localized ferromagnetic moment and itinerant holes that mediate the coupling through a *p-d Zener* interaction.^{28,41} Interstitial Mn atoms (Mn_i) act as double donors and couple antiferromagnetically to Mn_s , effectively compensating both electrically and magnetically the Mn_s moments.^{29,92} This interstitial compensation has been shown to, at every given Mn concentration, influence the Fermi level, the hole concentration, and the effective magnetization in (Ga,Mn)As thin films.^{29,39,51,92,199,216} Previous studies have focused on reducing the fraction of compensating interstitial impurities by careful synthesis optimization and post-growth treatments, aiming at improving the magnetization and the Curie temperature.^{22,25,29,51,92,100} (Ga,Mn)As is typically grown at several percent Mn by low-temperature molecular beam epitaxy (LT-MBE), and can be *activated* by post-growth thermal annealing treatment at temperatures close to growth-temperature, 160°C-200°C, reaching a maximum Curie temperature T_C close to ~ 200 K.^{22,25,100} While this thermal treatment promotes interstitial mobility and passivation at the surface, Mn out-diffusion is limited by the local structure of the Mn defects, which is concentration dependent and sets a lower bound for the minimum annealing temperature, and by an onset of low temperature substitutional segregation, setting an upper boundary (cf. section 5).^{60,65,92,101,102}

(Ga,Mn)Sb is another Mn-doped III-V **DMS** with similar properties to (Ga,Mn)As, which has been shown to contain lower magnetic compensation.^{80,81} This has been attributed to the absence of a compensating interstitial fraction, which may be a consequence of the larger lattice constant in these systems. However, a detailed understanding of the (Ga,Mn)Sb phase diagram is still lacking, as its synthesis into a dilute magnetic matrix remains challenging.^{82,83} MnSb ferromagnetic inclusions have been observed in (Ga,Mn)Sb layers, with large blocking temperatures and providing high superparamagnetic T_C , limiting substitutional Mn incorporation and ferromagnetic T_C .^{84–89}

Engineering Mn-doped III-V **DMS** composition has been extensively studied over the past decade as a possible route to improve T_C and effective magnetization. The introduction of small concentrations of other group V elements at the arsenic sites, has been observed to increase the tunability of quaternary

(Ga,Mn)(As,X) layers, by adjusting magnetic and electric properties, such as magnetic anisotropy, band gap, or even carrier concentration.^{68–71} Particularly, doping (Ga,Mn)As layers with P or Sb has been shown to add a weaker tendency for self-compensation, with the caveat of a degraded crystal quality, ultimately decreasing the effective Mn concentration.^{71,78,79} Additionally, *ab initio* studies demonstrated a linear decrease in T_C with increasing P doping.⁷⁷ On the other hand, new interesting functionalities appear with P and Sb doping, such as precise control and switching of the magnetic anisotropy in (Ga,Mn)(As,P) or the anisotropic magnetoresistance in (Ga,Mn)(As,Sb), through the fine tuning of epitaxial strain and/or alloy composition.^{68,70,72,73,103,104} Furthermore, new unexpected effects have been found such as magnetic domain-wall motion associated with carrier spin drift velocities in (Ga,Mn)(As,P).^{74–76}

Here we report on the thermal stability of Mn in III-V DMS using the emission channeling technique. We aim to understand the interplay between substitutional and interstitial diffusion, and how it determines the properties observed for the different III-V hosts, such as Mn_i compensation and formation, and segregation of MnAs and MnSb ferromagnetic inclusions.

7.3 Experimental details

In order to better comprehend the thermal stability and diffusion of Mn in Ga-Mn-V DMS we performed two different sets of emission channeling experiments using radioactive ⁵⁶Mn probes: (i) Mn lattice location and thermal stability in GaP, GaAs and GaSb substrates; (ii) Mn thermal stability in Ga-Mn-V ferromagnetic thin films. The first set of experiments addresses the lattice location and thermal stability of Mn dopants in commercial III-V semiconductor crystals, GaP, GaAs and GaSb as a function of annealing temperature up to 800°C. The second experimental set explored the thermal stability as a function of annealing temperature up to 500°C in (Ga,Mn)As, (Ga,Mn)(As,P), (Ga,Mn)(As,Sb) and (Ga,Mn)Sb thin films (25 nm in thickness) doped with an estimated concentration of 6% Mn. (Ga,Mn)(As,P) and (Ga,Mn)(As,Sb) films contained 30% P and 10% Sb, respectively. These thin films were grown by low-

temperature molecular beam epitaxy (LT-MBE) at Nottingham University,^{59, 100} and were grown on GaAs substrates, except (Ga,Mn)Sb which was grown on InAs.

Emission channeling uses radioactive isotopes as probes for investigating the local structure and lattice location of dopants or impurities in semiconductors.¹⁸⁰ These radioactive probes are implanted in the crystal, and their decay products, usually β^- and/or conversion electrons, are channeled at relativistic speeds through the crystallographic axes and planes. Anisotropic scattering of these electrons results in well-defined channeling or blocking effects, which are strongly dependent on the initial position of emitted particles. A dilute concentration ($< 0.05\%$) of radioactive ^{56}Mn (half-life $t_{1/2} = 2.56$ h) was implanted into the III-V semiconductors and Ga-Mn-V thin films. For lattice location of the ^{56}Mn probes, angular-dependent emission patterns were recorded along four main crystallographic axes ($\langle 100 \rangle$, $\langle 111 \rangle$, $\langle 110 \rangle$ and $\langle 211 \rangle$) using a position- and energy-sensitive detector, in the EC-SLI chamber at ISOLDE-CERN.¹⁸⁴ The thermal stability of ^{56}Mn probes was investigated differently within each experimental set: in the pure semiconductor substrates (samples a-c in Table 7.1) emission channeling patterns were acquired as a function of annealing temperature up to 800°C , in 10 minute steps of 50°C ; in ferromagnetic Ga-Mn-V thin films patterns were recorded only along the $\langle 211 \rangle$ direction up to 500°C . This approach allowed to keep the implanted fluence about a factor of 5 lower. All experiments were performed in high vacuum ($< 10^{-5}$ mbar), and following ^{56}Mn implantations at room temperature. In particular for the second experimental set, ^{56}Mn implantations were performed at an energy of 30 keV and at an angle of $\theta = 60^\circ$ in order to create implantation profiles located inside the thin films (25 nm thickness). Relevant emission channeling experimental details are described in Table 7.1. The emission channeling experimental data were subsequently fitted by theoretical emission patterns, calculated for a large variety of possible lattice sites and displacements using the *manybeam* formalism for electron channeling in single crystals.¹⁸⁰ Quantitative lattice location was provided by fitting the experimental patterns to theoretical ones using a two-dimensional χ^2 -minimization fit procedure.¹⁹² The effect of backscattered electrons that reach the detector and contribute with an isotropic background was estimated

#	sample	E [keV]	θ [°]	R_p [nm]	σ [nm]	fluence [cm ⁻²]	x_p [cm ⁻³]
a	GaP	50	17	37.1	18.1	9×10^{12}	1.8×10^{18}
b	GaAs ⁹⁴	50	17	31.3	16.8	2×10^{13}	4.6×10^{18}
c	GaSb	50	17	30.9	17.4	1×10^{13}	2.2×10^{18}
d	(Ga,Mn)As	30	60	12.3	8.1	2×10^{12}	8.8×10^{17}
e	(Ga,Mn)(As,P)	30	60	13.0	8.5	2×10^{12}	9.7×10^{17}
f	(Ga,Mn)(As,Sb)	30	60	12.6	8.4	2×10^{12}	7.6×10^{17}
g	(Ga,Mn)Sb	30	60	12.3	8.1	2×10^{12}	8.6×10^{17}

Table 7.1: Sample and implantation details. All implantations were performed at room temperature. Implantation energy and angle are denoted, respectively, by E and θ . Peak concentration (x_p), projected ion range (R_p) and straggling (σ) were estimated using the SRIM-2008 code.¹⁹¹

through Geant4 simulations of electron scattering,^{188,189} and then taken into account by multiplying the site fractions with a correction factor. This procedure determines the best fitting sites for each pattern together with a *site-fraction*, the amount of ⁵⁶Mn radioactive probes fitted per site.¹⁸⁶

Performing the emission channeling for various annealing steps allowed us to further investigate substitutional and interstitial Mn diffusion in Ga-Mn-V DMS, by determining the site fractions as a function of annealing temperature.^{90,94,179} These site fractions will most likely differ from those of the stable isotopes incorporated during growth, since ion implantation has different kinetics than doping during LT-MBE growth. However, the probes' diffusion can accurately reproduce that of the Mn dopants incorporated during growth, as once the implanted atoms are at rest, their behavior does not depend on their history or isotope.

7.4 Results

This section addresses the emission channeling results on the lattice location and thermal stability of ⁵⁶Mn in both experimental sets: sections 7.4.1 and 7.4.2 focus

on the pure semiconductors GaP, GaAs and GaSb, and sections 7.4.4 and 7.4.4 on the Ga-Mn-V ferromagnetic thin films.

7.4.1 Mn lattice location in GaP, GaAs and GaSb

Previous research established substitutional and interstitial sites as the two preferential lattice sites occupied by Mn in GaAs, with the former incorporated as an acceptor and the latter as a donor. Furthermore, emission channeling experiments of ^{56}Mn in GaAs showed a major fraction of Mn probes occupying Ga-substitutional sites (S_{Ga}), with a minor fraction in tetrahedral sites coordinated by As nearest neighbor (T_{As}).^{90,94} The experiments described below also show a larger fraction of radioactive ^{56}Mn probes in Ga-substitutional sites (S_{Ga}) for both GaP and GaSb semiconductors, with minor interstitial fractions in T_{B} or S_{B} sites, where A and B stand for cation and anion in the crystal, respectively. Accordingly, fitting emission channeling experimental patterns to theoretical S_{A} patterns gives by far the best agreement, for a one site fit. By including additional sites in the fitting routine we were able to refine the best fit for each semiconductor crystal: for GaSb, this was found for $S_{\text{A}}+T_{\text{B}}$ double occupancy patterns, with a larger fraction of radioactive probes occupying S_{A} sites and a smaller one T_{B} sites; for GaP the best fit was found for the $S_{\text{A}}+S_{\text{B}}$ patterns, with a major fraction in Ga-substitutional and minor in P-substitutional. While adding a third interstitial lattice site to the fitting routine results in estimated fractions below 5% for GaSb and GaAs, in GaP a statistically relevant improvement is observed: χ^2 improves by 10% when fitting the $S_{\text{A}}+S_{\text{B}}+T_{\text{B}}$ triple site occupancy, with minor fractions in the two latter sites.

Fig. 7.1 illustrates the good match between experimental and simulated patterns for both GaP and GaSb experiments, by comparing the normalized experimental β^- emission yields taken at 150°C along the four measured crystallographic directions (a-d, i-l) with their respective best fits (e-h, m-p). Accordingly, for GaP the fits yielded 61% of ^{56}Mn atoms in S_{Ga} sites, with 28% and 11% in S_{P} and T_{P} , respectively. Fits in the GaSb experiment yielded ^{56}Mn fractions of 68% in S_{Ga} sites and 20% in T_{Sb} .

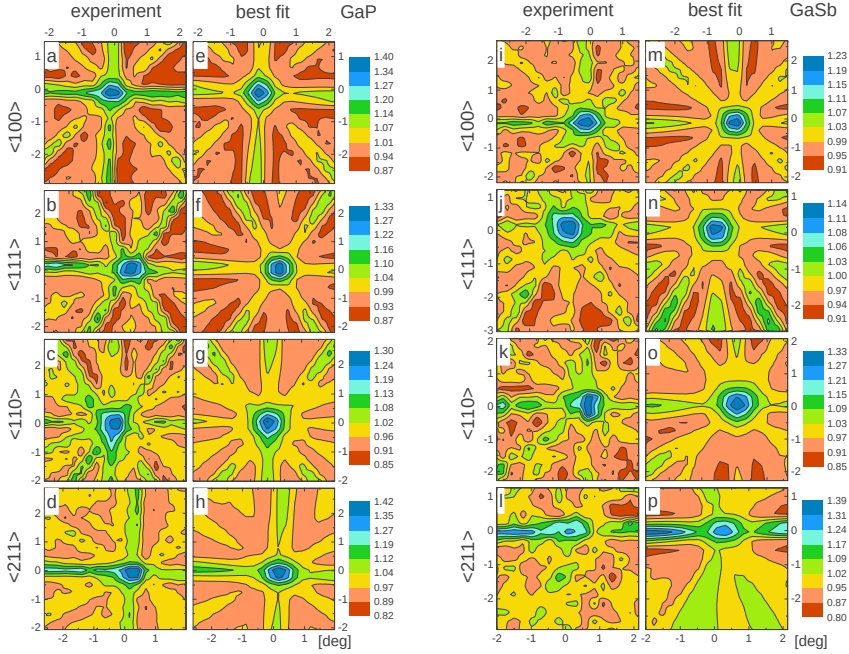


Figure 7.1: (a)-(d) and (i)-(l) Normalized experimental β^- emission channeling patterns in the vicinity of $\langle 100 \rangle$, $\langle 111 \rangle$, $\langle 110 \rangle$ and $\langle 211 \rangle$ directions in, respectively, GaP (left) and GaSb (right), after annealing at 150°C , and corresponding best fits (e)-(h) and (m)-(p).

There is a clear preference for Mn to occupy S_A substitutional and T_B interstitial sites in all three semiconductors, GaP, GaAs and GaSb, due to their similar local structure in a $F\bar{4}3m$ *zincblende* crystal lattice. Additionally, the presence of Mn on P sites in GaP indicates that there is some additional effect contributing to its incorporation in this material upon implantation.

The incorporation of Mn in anion substitutional sites is poorly understood, with little theoretical studies considering its existence in III-V semiconductors, and only observed in a few experimental studies in GaN.^{194–196,221} Using x-ray absorption spectroscopy XAFS, Takano *et al.* observed fractions of up to 75% of Mn dopants occupying N-substitutional sites in *zinc-blende* GaN films grown by LT-MBE in N-poor conditions.²²¹ In this study N vacancies were intentionally utilized as donor dopants, and arguably resulted in high enough

fraction of N-substitutionals to allow XAFS detection. Anion-substitutional Mn atoms in GaN have also been observed in previous emission channeling investigations,^{194,195} and were found to be thermally stable up to high annealing temperatures, 900°C.

The observation of anion substitutional Mn atoms in emission channeling experiments, such as the one reported here for Mn in GaP, can be partly attributed to the non-equilibrium nature of ion implantation. Upon implantation, a high concentration of anion vacancies is created and is likely to facilitate Mn incorporation in anion sites. However, this explanation is not sufficient as, under very similar experimental conditions, other emission channeling experiments in GaN crystals yield different results: while experiments using ⁶¹Co isotopes also observed anion substitution,¹⁹⁶ the same did not occur for ⁵⁹Fe.^{193,222} Mn, Co and Fe are 3d transition metals with similar atomic mass, and therefore, similar incorporation kinetics and defect creation. This suggests that the incorporation of Mn atoms into the anion-substitutional sites points towards a particular affinity of Mn dopants to the lattice site. Similarly to cation antisites, fairly common defects in III-V semiconductors,^{223–225} Mn impurities could be incorporated as anion-substitutionals under non-equilibrium conditions at different charge states, favoring coupling to Ga atoms instead of Group V elements. Further investigations are necessary on the nature of the Mn anion substitutional in III-V semiconductors, particularly on their formation energies at various charge states and in the presence of a sufficient amount of anion vacancies.

7.4.2 Mn thermal stability in GaP, GaAs and GaSb

Investigating the occupied ⁵⁶Mn sites as a function of annealing temperature provides insight on Mn thermal stability across the selected III-V semiconductors. Figs. 7.2(a)–(c) plot, for each annealing temperature, the best fitting site-fractions from emission channeling analysis for GaP, GaAs, and GaSb, respectively. The variation of site-fractions within an experiment can be attributed to one of two effects: (i) implantation damage recovery, or (ii) diffusion of Mn probes. As was established previously, most of the radioactive

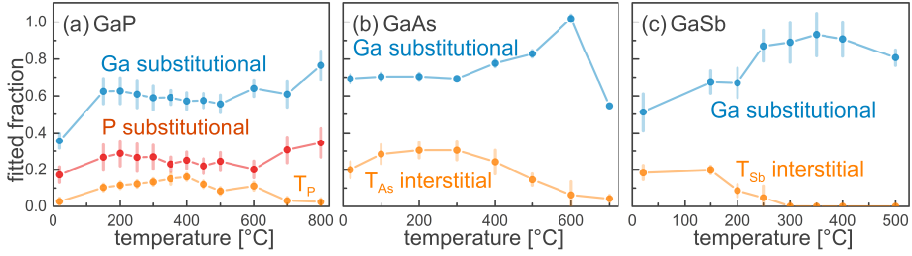


Figure 7.2: Fitted fractions of implanted ^{56}Mn in (a) GaP, (b) GaAs⁹⁴ and (c) GaSb (averaged over $\langle 110 \rangle$ and $\langle 211 \rangle$ directions). The interstitial Mn stability significantly decreases from GaP to GaAs to GaSb.

Mn probes occupy Ga-substitutional sites. At low annealing temperatures, a general increase of S_{Ga} fractions is observed for GaP and GaSb, and can be attributed to implantation damage recovery. During ^{56}Mn implantation many defects are created, such as vacancies and disordered regions, which trap the radioactive probes. Due to the resulting irregular crystallographic potential, electrons emitted from these regions will not be channeled, contributing to the pattern as an isotropic background. By annealing at low temperatures, these defects are partially annealed, which improves the channeling effects for all probe atoms (cf. section 5.6).

Site-fractions can also change as a function of annealing temperature due to diffusion of ^{56}Mn probes within the crystal. This can usually be attributed to two basic mechanisms: on the one hand, diffusion can lead to the incorporation of probes in structurally different lattice sites, which is often the result of a comparably small number of diffusion jumps; on the other hand, long-range diffusion will eventually significantly broaden the implantation profile. The latter effect will cause probes to either reach the sample surface, where emitted electrons do not channel any longer, or escape to the bulk of the sample, where emitted electrons dechannel due to excessive path lengths out of the sample. As an example of conversion between lattice sites, Fig 7.2(b) shows a decrease of T_{B} interstitial fractions at temperatures $> 400^\circ\text{C}$, a direct consequence of Mn_i becoming mobile. The diffusing interstitials combine with Ga-vacancies in the GaAs crystal, becoming substitutionals and increasing the S_{Ga} site-fractions, as is observed in Fig. 7.2(b). This effect is further detailed in Refs.^{90,94} Conversely,

at 700°C the Mn_s site-fraction decreases significantly due to long-range Mn diffusion. However, only diffusion jumps parallel to the surface normal should contribute to this effect, since diffusion in planes parallel to the surface will not broaden the Mn depth profile.

Fig. 7.2 shows remarkably similar features between the three investigated III-V semiconductors: large substitutional fractions which remain relatively stable up to the highest annealing temperatures in each experiments; and small interstitial fractions which decrease with increasing annealing temperature. Moreover, Mn impurities in P-substitutional sites in GaP appear to have similar thermal stability to Ga-substitutional sites.

In a similar fashion to our experiments described in section 5.4.2, the thermal stability of both Ga-substitutional and interstitial Mn atoms in all three semiconductors can be characterized by a modified Arrhenius model and an activation energy for diffusion E_a . Assuming an interstitial diffusion model, the fraction $f(T, \Delta t)$ of Mn occupying interstitial T_B sites after an annealing step at a temperature T of duration Δt is given by

$$f(T, \Delta t) = f_0 \exp(-\mu_0 \Delta t / N \exp(-E_a / k_\text{B} T)) \quad (7.1)$$

where f_0 is the interstitial T_B fraction before the annealing step; μ_0 is the attempt frequency, which we take as 10^{12} s^{-1} , of the order of the lattice vibrations; k_B is the Boltzmann constant; and N is the average number of jumps before a Mn_i atom combines with a Ga-vacancy.²²⁶ In this expression, N cannot be determined independently from E_a , but minimum and maximum values can be deduced based on two extreme and opposite scenarios before the mobilization of Mn_i : (i) there is an immobile V_Ga within one jump of every Mn_i atom, and (ii) Mn_i and V_Ga are distributed evenly and independently. In the first scenario, Mn_i requires only one jump to convert into Mn_s , $N = 1$; in the second, we consider a sufficient number of jumps such that the average diffusion width projected in one dimension equals the implantation depth, resulting in $N = 18000$ for GaSb and $N = 26000$ for GaP. Inserting these values in the $f(T, \Delta t)$ equation (7.1) yields activation energies of $E_a = 1.0 - 1.4 \text{ eV}$ and $E_a = 2.0 - 2.8 \text{ eV}$, for GaSb and GaP, respectively.

sample	substitutional		interstitial	
	$T_{1/2}$ [°C]	E_a^s [eV]	$T_{1/2}$ [°C]	E_a^i [eV]
GaP	> 800	> 3.4	600 – 700	2.0 – 2.8
GaAs	600 – 700	3.0	400 – 500	1.7 – 2.3
GaSb	> 500	> 2.4	150 – 200	1.0 – 1.4

Table 7.2: Estimated activation energies E_a for substitutional and interstitial Mn diffusion in GaP, GaAs and GaSb. $T_{1/2}$ represents the temperature range at which fitted fractions reduce to $f_0/2$. Since $T_{1/2}$ temperatures were not reached for substitutional fractions in both GaP and GaSb, a lower bound for E_a^s is presented.

The activation energy for Mn substitutional diffusion can also be estimated and compared between the three III-V semiconductors. A decrease in Ga-substitutional fraction in Fig. 7.2 usually indicates either (i) a long-range diffusion to the sample bulk or surface, or (ii) clustering within the implanted layer. At the very low Mn concentration range detailed in these experiments, the first phenomenon is the most likely scenario for Mn_s diffusion. Similar to the model employed for ^{56}Mn in GaAs in Refs. [90, 94], the diffusion of substitutional Mn can be modeled by a Frank-Turnbull mechanism: Mn atoms jump from their substitutional sites, diffusing interstitially until trapped by Ga vacancies V_{Ga} , becoming substitutional Mn_s . Assuming a constant V_{Ga} concentration, this diffusion can also be modeled by an Arrhenius curve, and the activation energy given by the binding energy between the diffusing Mn and V_{Ga} plus the migration energy of interstitial Mn diffusion. This behavior can then be modelled using Eq. (7.1), where N is the number of steps until ^{56}Mn probes are either at the surface or too deep to contribute with measurable channeling effects. Assuming only a low concentration of Ga vacancies persists in all III-V at these temperatures, N can be safely approximated to only one step.

Whereas this model can be easily applied to estimate the activation energy for substitutional diffusion in GaAs, the emission channeling data presented in Fig. 7.2 do not display a (significant) decrease in Mn_s fractions for GaP (GaSb). Nevertheless, an estimate for the minimum E_a for Mn_s mobility can be obtained by assuming that the next annealing step, 900°C for GaP and 600°C

for GaSb, would drastically decrease its site-fraction.

Table 7.2 compiles the estimated activation energies and shows a clear decrease for both substitutional and interstitial diffusion from GaP to GaAs to GaSb. This decrease can be directly linked to the increase of interstitial Mn mobility, which is a consequence of lower energetic barriers that Mn atoms in T_B sites have to overcome. The height of these barriers is largely affected by the local structure of the interstitial site, i.e. the atomic packing and the lattice constant of the host. As the bond strength between the Ga atoms and the group V elements increases from Sb to As to P, the lattice constant decreases (from 6.10 Å in GaSb, to 5.65 Å in GaAs, to 5.45 Å in GaP),⁴⁵ increasing the atomic packing and the energetic barriers surrounding the T_B site.

Similar trends are observed in the Mn-doped thin films, as described next.

7.4.3 Mn Lattice location in Ga-Mn-V

In the previous section we identified the Mn lattice location in GaP, GaAs and GaSb crystals as the Ga-substitutional site (S_{Ga}) and the tetrahedral interstitial site coordinated by the anion P, As or Sb (T_B). Additionally, the same lattice sites were found in chapter 4 for ferromagnetic (Ga,Mn)As thin films, where we unambiguously identified the tetrahedral interstitial site coordinated by As (T_{As}) as the preferred interstitial site when compared to (T_{Ga}). In a similar fashion, the experiments described here on Ga-Mn-V ferromagnetic thin films also yielded the $S_A + T_B$ double occupancy patterns as the best fitting sites for all samples. As an example, we will focus on the identification of Mn lattice sites in (Ga,Mn)Sb using a similar approach to the one previously described in sections 4 and 5 for (Ga,Mn)As films. The same procedure was followed for experiments (d)-(f) in Table 7.1.

Figs. 7.3(a)-(h) display the experimental emission patterns of the (Ga,Mn)Sb experiment at room temperature, along the four measured directions ((a)-(d)), together with their respective best fits to theoretical patterns ((e)-(h)). Additionally, Figs. 7.3(i)-(m) illustrate how the (110)-planar channeling mirror asymmetry, measured in the vicinity of the $\langle 211 \rangle$ direction (horizontal plane in

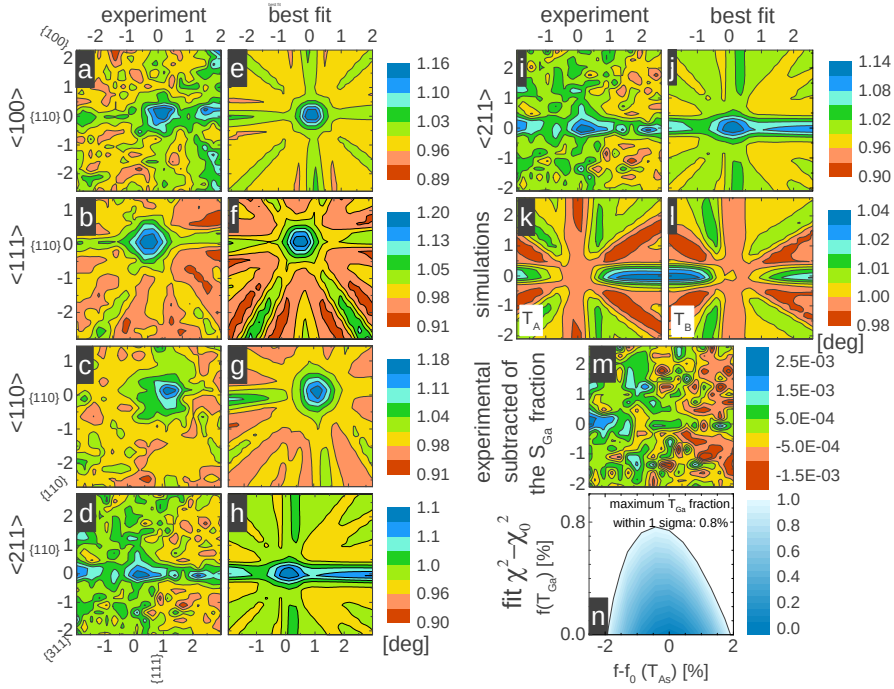


Figure 7.3: (a)-(d) Normalized experimental β^- emission channeling patterns at room temperature (RT) in the vicinity of $\langle 100 \rangle$, $\langle 111 \rangle$, $\langle 110 \rangle$ and $\langle 211 \rangle$ directions in (Ga,Mn)Sb, and best fits (e)-(h), corresponding to 22% of probes in S_{Ga} sites and 10% in T_{Sb} . (i) Experimental emission channeling pattern (RT) in the vicinity of $\langle 211 \rangle$ in (Ga,Mn)Sb, and (j) respective best fit. (k)-(l) Calculated T_{Ga} and T_{Sb} patterns for (Ga,Mn)Sb. (m) Experimental pattern (i) subtracted by fitted substitutional S_{Ga} pattern, demonstrating the good visual agreement with (l) rather than (k). (n) Difference between the chi square of the fit and the best fit chi square, $\chi^2 - \chi_0^2$, with χ_0^2 being the value for the best fit, for (Ga,Mn)Sb at room temperature. See text for further explanation.

the figure), allows us to distinguish between T_{Ga} and T_{Sb} sites. Subtracting the fitted substitutional component from the experimental data yields a residual (110)-planar channeling asymmetry which quantitatively corresponds to that of T_{Sb} (Fig. 7.3(l)), i.e. with stronger channeling on the left versus the right of figure, in contrast to what would be expected for T_{Ga} sites. Fig. 7.3(n) shows the sensitivity of emission channeling in the quantitative analysis of the ^{56}Mn interstitial location in (Ga,Mn)Sb for the case of T_{Ga} versus T_{Sb} occupancy, by plotting the difference between the chi square of the fit (χ^2) and the best fit chi square (χ_0^2) as the fractions on T_{Ga} and T_{Sb} are varied in the vicinity of the best fit values χ_0^2 , 10% for T_{Sb} and 0% for T_{Ga} , leaving the remaining fit parameters free. The dark line contour corresponds to $\chi^2 - \chi_0^2 = 1$, giving standard deviations of 2% for the T_{Sb} fraction and of 0.8% for T_{Ga} . In other words, within the technique's sensitivity the T_{Ga} occupancy can be considered negligible. The main finding here is that Mn occupies mainly Ga-substitutional sites (S_{Ga}) and T_B interstitial sites, with negligible (if any) T_{Ga} occupancy.

7.4.4 Mn thermal stability in Ga-Mn-V

Analogous to the thermal stability analysis described in section 7.4.2 for undoped GaP, GaAs and GaSb, the fitted ^{56}Mn fractions in the various Ga-Mn-V thin films as a function of annealing temperature are investigated here. As mentioned previously, two effects can drive the lattice site occupancy of ^{56}Mn : (i) implantation damage recovery (ii) and Mn diffusion. In the experiments presented here we observe both effects, with (i) most significantly at lower annealing temperatures and (ii) at higher ones. Furthermore, since the samples contain 6% of stable ^{55}Mn , the diffusion of interstitial and substitutional Mn will also lead to Mn segregation.

Figs. 7.4(a)-(d) depict the fitted site fractions as a function of annealing temperature obtained for all emission channeling experiments on the four DMS thin films along the $\langle 211 \rangle$ direction. Measurements along the $\langle 211 \rangle$ direction were selected due to their high sensitivity to the $S_A + T_B$ double occupancy, as demonstrated above. Moreover, it is the relative evolution of site fractions with annealing temperature which accurately represents the thermal stability of

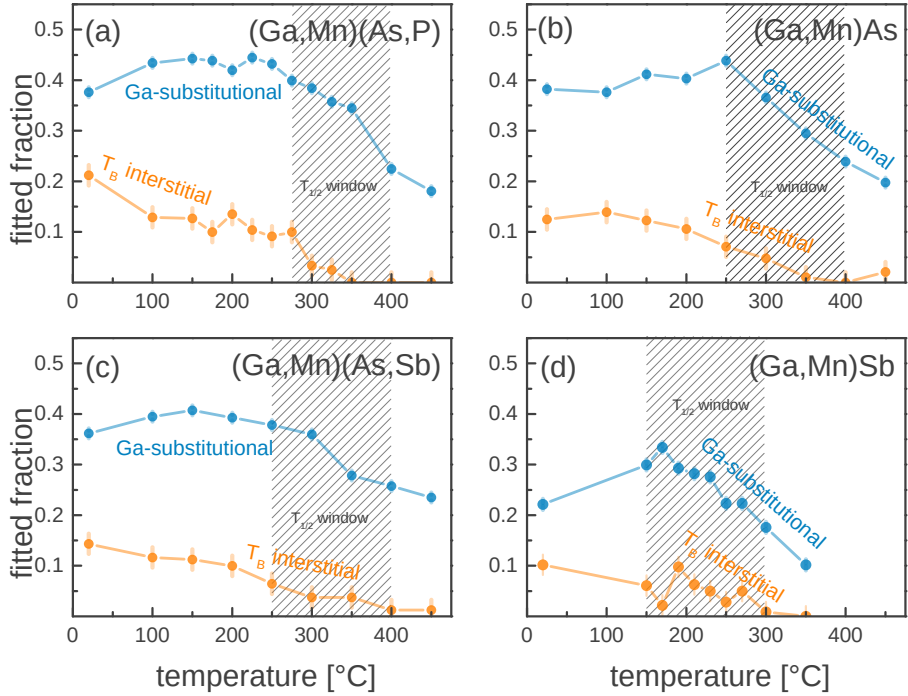


Figure 7.4: Fitted emission channeling fractions of implanted ^{56}Mn probes as a function of annealing temperature for (a) $(\text{Ga,Mn})(\text{As,P})$, (b) $(\text{Ga,Mn})\text{As}$, (c) $(\text{Ga,Mn})(\text{As,Sb})$, and (d) $(\text{Ga,Mn})\text{Sb}$. The gray-shaded areas illustrate the $T_{1/2}$ temperature windows between the $T_{1/2}$ points of interstitial and substitutional diffusion. See text for a detailed explanation.

occupied Mn lattice sites, and it can be determined with higher accuracy than the absolute fractions of interstitial and substitutional Mn in Ga-Mn-V thin films.

A first trend observed in Fig. 7.4 is the significantly lower temperatures at which substitutional and interstitial ^{56}Mn probes become mobile when compared to the ultra-dilute case depicted in section 7.4.2. More specifically, the incorporation of a few percent of stable Mn into these systems lowers diffusion barriers, which is clearly visible when comparing the curves of $(\text{Ga,Mn})\text{As}$ and $(\text{Ga,Mn})\text{Sb}$ in Fig. 7.4 to the corresponding curves of GaAs and GaSb in Fig. 7.2. This has also been observed specifically for $(\text{Ga,Mn})\text{As}$ films in chapter 5, and has been

attributed to a concentration dependence on the diffusion of charged interstitials. This diffusion model is adapted to the present case below.

A second general trend observed in Figs. 7.4(a)-(d) is the decrease of ^{56}Mn thermal stability in both substitutional and interstitial sites from $(\text{Ga,Mn})(\text{As,P})$ to $(\text{Ga,Mn})\text{As}$ to $(\text{Ga,Mn})\text{Sb}$. To observe this decrease, $T_{1/2}$ windows are illustrated for each DMS thin film, and represent the temperature range between the $T_{1/2}$ points of interstitial and substitutional diffusion. Note that these windows are extracted from the $T_{1/2}$ ranges defined for the diffusion model below (cf. Table 7.3), which represent the temperature range at which fitted substitutional or interstitial fractions reduce to half ($f_0/2$). The $T_{1/2}$ windows can serve as a rough guide for the annealing temperatures where it is possible to significantly reduce the interstitial Mn without affecting too severely the substitutional Mn. As observed in Figs. 7.4(a)-(d), these windows shift towards lower annealing temperatures across the series. This trend corresponds to the slight decrease in Mn thermal stability from $(\text{Ga,Mn})(\text{As,P})$ to $(\text{Ga,Mn})\text{As}$ to $(\text{Ga,Mn})(\text{As,Sb})$, also observed in the experiments described in section 7.4.2 for the undoped semiconductors GaP, GaAs and GaSb.

In particular, this effect is enhanced for $(\text{Ga,Mn})\text{Sb}$, where the $T_{1/2}$ window shifts to the lowest of the four experiments. The weaker bond strength between Ga and Sb atoms decreases energy barriers for Mn interstitial diffusion, and, combined with the higher mass of Sb atoms, effectively adds to the dechanneling of electrons emitted from ^{56}Mn probes. As an additional consequence, fitted fractions observed for $(\text{Ga,Mn})\text{Sb}$ in Fig. 7.4(d) are also the lowest of the experimental set.

The two trends can be quantitatively illustrated through the activation energies for diffusion of both interstitial and substitutional Mn depicted in Table 7.3. Here, conservative estimates for these activation energies were calculated using a similar approach to the one described above in section 7.4.2 for the ultra-dilute case in GaP, GaAs and GaSb. The resulting activation energies for substitutional and interstitial diffusion, E_a^s and E_a^i , respectively, can be further modeled by a diffusion model similar to the one described in section 5.4.2 for $(\text{Ga,Mn})\text{As}$ crystals.

sample	substitutional		interstitial	
	$T_{1/2}$ [°C]	E_a^s [eV]	$T_{1/2}$ [°C]	E_a^i [eV]
(Ga,Mn)(As,P)	400 – 450	2.1	275 – 300	1.3 – 1.7
(Ga,Mn)As	400 – 450	2.1	250 – 300	1.2 – 1.6
(Ga,Mn)(As,Sb)	400 – 450	2.1	250 – 300	1.2 – 1.6
(Ga,Mn)Sb	300 – 350	1.8	150 – 170	1.0 – 1.3

Table 7.3: Estimated activation energies E_a for substitutional and interstitial Mn diffusion in Ga-Mn-V films. $T_{1/2}$ represents the temperature range at which fitted fractions reduce to $f_0/2$.

In the ultra-dilute regime (cf. section 7.4.2), the Mn interstitial can be assumed to diffuse as a free, isolated interstitial,^{90,94} as the very low local Mn concentration drives down the probability for a Mn_i to occupy a position near a Mn_s . Accordingly, the activation energy for free interstitial diffusion is directly related to a *migration energy*, E_m , between adjacent interstitial sites, i.e. the energy required for the ^{56}Mn probe to jump between neighboring T_A and T_B interstitial sites. In chapters 4 and 5 we showed that the $\text{T}_A \rightarrow \text{T}_B$ barrier is already overcome at room temperature in ferromagnetic (Ga,Mn)As films, since Mn_i only occupies T_B sites even after thermal annealing at 200°C. Hence, we can attribute E_m to the diffusion along the path $\text{T}_A \rightarrow \text{T}_B \rightarrow \text{T}_A$, and connect it with the free interstitial diffusion in the ultra-dilute case, $E_a^i = E_m$.

A free interstitial diffusion model is, however, incomplete in the Mn concentration regime investigated here, as interstitial Mn impurities are more likely to be trapped in complexes with substitutional Mn atoms. This results in significant fractions of complexes between substitutional and interstitial Mn atoms, such as pairs ($\text{Mn}_s\text{-Mn}_i$) and triplets ($\text{Mn}_s\text{-Mn}_i\text{-Mn}_s$), which contribute to the activation energy for Mn_i diffusion with an additional energy barrier, E_b^i . Thus, E_b^i represents the energetic barrier that Mn_i has to overcome in order to break its bond with substitutional Mn atoms. This energy barrier is largely determined by the Coulomb interaction between oppositely charged Mn_s^- and Mn_i^{2+} , and should increase with the number of Mn_s involved in the complex. *Ab initio* calculations predict this increase in (Ga,Mn)As layers, with $E_b^{\text{pair}} = 0.49$ eV for the $\text{Mn}_i\text{-Mn}_s$ bond, and $E_b^{\text{triplet}} = 0.81$ eV for $\text{Mn}_s\text{-Mn}_i\text{-Mn}_s$ bonds.⁶⁵ From

a purely statistical approach the abundance of these pairs and triplets can be estimated using the model described in Ref. 198, assuming the binding of an interstitial Mn atom to substitutional complexes. Accordingly, considering a random distribution of substitutional Mn within the films, at a concentration of 6% Mn, the fractions of isolated substitutional atoms (x_s) and of pairs of neighboring substitutional Mn atoms (x_{s-s}) as a function of Mn concentration x can be estimated as $x_s = 48\%$ and $x_{s-s} = 24\%$, respectively, with the remaining 28% in higher complexity configurations, such as three substitutionals. The binding energy barrier is expected to increase the total activation energy for diffusion at this concentration, $E_a^i = E_m + E_b^i$.

In chapter 5, a third contribution Δ to the activation energy for interstitial diffusion was introduced for the several percent Mn content regime. This contribution results from the electrostatic interaction between the diffusing Mn species and the more distant substitutional Mn atoms. While binding to substitutional Mn increases the activation energy for interstitial diffusion by E_b^i , the Coulomb interaction between the diffusing Mn_i and the neighboring substitutional Mn atoms will decrease E_a^i by Δ . This effect becomes relevant at Mn concentrations in which the distance between substitutional atoms is smaller than the distance required for an interstitial atom to diffuse away from its initial lattice site.^{227,228} Within a percolation cluster of Mn_s atoms, the Coulomb interaction energy between Mn_s^{2+} and Mn_i^- at a distance of 10 Å can be estimated as $\Delta \approx 0.2$ eV in a 6% Mn (Ga,Mn)As sample, taking the GaAs dielectric constant (13.2). However, within a sphere of radius 10 Å from a Mn_i atom there are at least six Mn_s , resulting in possible potential modifications of the order of $\Delta \approx 1.2$ eV. A similar estimation can be performed for (Ga,Mn)Sb films, yielding an interaction energy of the order of $\Delta \approx 1.1$ eV. The potential modifications compete with E_b^i , and are expected to reduce the activation energy for interstitial diffusion, $E_a^i = E_m + E_b^i - \Delta$.

Lastly, the diffusion of substitutional Mn can be assumed to be of the Frank-Turnbull type, where thermally activated Mn_s first leaves its substitutional lattice site, diffusing as an interstitial until it encounters the next stable trap. In the ultra-dilute regime, these traps are usually Ga-vacancies, whereas in the percent Mn regime, regions with segregated Mn can also be considered as traps.

sample	ΔE_a^{s-i} [eV]
(Ga,Mn)(As,P)	0.4 – 0.8
(Ga,Mn)As	0.5 – 0.9
(Ga,Mn)(As,Sb)	0.5 – 0.9
(Ga,Mn)Sb	0.5 – 0.8

Table 7.4: Difference between estimated activation energies for substitutional and interstitial diffusion.

The activation energy for substitutional diffusion can then be split into two terms, one consisting of the binding energy of Mn to the substitutional site, E_b^s , and another being the activation energy for interstitial diffusion, E_a^i . The total activation energy for substitutional diffusion can then be described as $E_a^s = E_b^s + E_a^i$.

From the activation energy for substitutional Mn diffusion in Table 7.3, the binding energy of Mn to the substitutional site, E_b^s , can be estimated by subtracting E_a^i from E_a^s , i.e. $\Delta E_a^{s-i} = E_a^s - E_a^i = E_b^s$. This difference is represented in Table 7.4, resulting in a rather constant ΔE_a^{s-i} for all thin films. In particular, while the E_a^s estimation yielded different values for (Ga,Mn)As and (Ga,Mn)Sb films, 2.1 eV and 1.8 eV, respectively, calculated E_b^s values remain within the same energy range. Consequently, in these 6% Mn-doped systems the nature of the anion (P, As, or Sb) does not seem to have a large influence on the binding energy of Mn to Ga-substitutional sites. The main drive for the decrease in activation energy from (Ga,Mn)As to (Ga,Mn)Sb must derive from contributions to the interstitial diffusion, E_a^i .

In sections 4.4 and 7.4.3 we observed T_B as the best fitting interstitial lattice site occupied by Mn impurities in both (Ga,Mn)As and (Ga,Mn)Sb. While this lattice site was observed as the most stable for both materials, its energy barrier differs between T_{As} and T_{Sb} . The stronger binding between Ga and As atoms in (Ga,Mn)As, compared to Sb in (Ga,Mn)Sb, directly results in a tighter atomic packing around the T_{As} site, increasing the energy barriers which Mn_i needs to overcome.^a This has a direct consequence on the E_m contribution to

^aIn analogy, the lattice parameter of GaSb is about 10% larger than GaAs.⁴⁵

the activation energy for interstitial diffusion, as it defines the diffusion between interstitial sites ($T_A \rightarrow T_B \rightarrow T_A$).

7.5 Discussion and conclusion

In the studies presented here we have observed two general trends in both pure III-V semiconductors and Mn-doped Ga-Mn-V [DMS](#): Mn thermal stability decreases as a function of (a) increasing Mn concentration, and of (b) decreasing bond strength between Mn and the group V element. The first has been described for GaAs and (Ga,Mn)As in [chapter 5](#), where the addition of Mn introduces a complex interplay between interstitial and substitutional stability. While Mn_{g} provides both the magnetic moment and the spin-polarized holes, which mediate the ferromagnetic interaction, Mn_{i} acts as a double donor and compensating defect. Thermal annealing at temperatures close to growth temperature results in partial out-diffusion of Mn_{i} . This process is limited, on the one hand, by the thermal stability of interstitials, particularly when in complexes with substitutional Mn atoms, introducing a lower limit for annealing temperature, and, on the other hand, by segregation of substitutional Mn atoms into MnAs nanoclusters (cf. [chapter 6](#)).

The addition of several percent group V elements does not appear to contribute to a more favorable Mn thermal stability, which decreases with decreasing bond strength between Mn and group V elements (trend b). In particular, the Mn thermal stability is strikingly similar across (Ga,Mn)(As,P), (Ga,Mn)As, (Ga,Mn)(As,Sb) thin films, with only a slight increase in interstitial Mn stability in the first. The slightly higher thermal stability in (Ga,Mn)(As,P) can potentially decrease the annealing window for interstitial out-diffusion, as well as lead to a larger interstitial fraction during growth. Consequently, while these effects may translate into lower T_C and magnetization in (Ga,Mn)(As,P),^{[72](#),[77](#)} they may also play an important role in other material properties, such as persistence of magnetic anisotropy,^{[73](#),[104](#)} or magnetic domain wall motion.^{[75](#)} On the other hand, the small percentage of Sb introduced in (Ga,Mn)(As,Sb) did not result in any change to either substitutional or interstitial thermal stability.

Sb-doping, however, has been observed to reduce crystal quality,⁷¹ effectively hindering T_C increase through thermal annealing.

Finally, the two trends outlined above provide a fundamental description for some structural and magnetic properties observed in (Ga,Mn)Sb. The Mn thermal stability in (Ga,Mn)Sb is the lowest among the probed materials, particularly due to the weaker bond strength between Mn and Sb atoms compared to Mn-As. This resulted in lower activation energies for both substitutional and interstitial diffusion, which provide, respectively, a smaller energetic barrier for Mn segregation, but also for interstitial formation. The first is evident by the presence of MnSb nanoclusters upon growth of (Ga,Mn)Sb layers,^{86,87} currently challenging a dilute incorporation of Mn. The second reflects the low thermal stability of interstitial Mn in (Ga,Mn)Sb. If Mn_i is mobile during LT-MBE growth, it is possible that it already out-diffuses during this process resulting in low or even non-compensated layers.⁸¹ The absence of interstitial impurities in (Ga,Mn)Sb layers was observed through magnetometry SQUID measurements, and is detailed in supplementary information (cf. section 7.6).

This work addressed the lattice location and thermal stability of Mn in GaP, GaAs and GaSb semiconductors and in ferromagnetic Ga-Mn-V thin films, doped with 6% Mn and a few percent of P or Sb. The majority of Mn atoms was found to substitute Ga sites, and a minor fraction occupy tetrahedral interstitial sites coordinated by the group V element as nearest neighbor. The thermal stability of both substitutional and interstitial Mn decreases from the ultra-dilute to the Mn-doped concentration range. We attribute this decrease to the stronger interaction between neighboring charged defects as the Mn concentration is increased. While the Coulomb interaction between nearest neighbor substitutional and interstitial Mn favors a larger thermal stability, it is countered by the interaction between the next nearest neighbors, ultimately resulting in a substantial decrease at larger Mn concentrations. Additionally, a significant decrease in Mn thermal stability has also been observed across both III-V semiconductors and Ga-Mn-V DMS as the anion changes from P to As to Sb, and can be directly attributed to the smaller packing as lattice constant increases.

Acknowledgments

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7.6 Supplementary information

Fig. 7.4(d) (Ga,Mn)Sb in the main text shows that the Mn interstitial fraction has significantly decreased after thermal annealing at $\sim 170^\circ\text{C}$. At the same instance as this decrease, the substitutional Mn fraction increases. This effect is likely due to the diffusion of interstitial probes, reflecting their mobility at this temperature, followed by recombination with the Ga-vacancies created during implantation, increasing substitutional ^{56}Mn fractions in (Ga,Mn)Sb. In the following annealing steps, substitutional fractions decrease (Mn_s becomes mobile), reflecting the diffusion of these probes according to the diffusion model described in the main text. However, since Mn diffuses through interstitial sites, we observe an increase in Mn_i fractions at these temperatures as shown in Fig. 7.4(d), resulting from the short annealing time.

The low thermal stability of interstitial Mn in (Ga,Mn)Sb may result in its out-diffusion during growth, resulting in non-compensated systems. Fig. 7.5 plots the effective magnetization per Mn atom in the four Ga-Mn-V thin films investigated in this study. The effective magnetization estimation was performed considering sample composition, mass, density and total magnetization. Oxidation effects could not be excluded from this estimation. Substitutional Mn in (Ga,Mn)As and (Ga,Mn)Sb has a theoretical effective magnetization of $4.0 \mu_B/\text{Mn}$.²⁸ Accordingly, a larger effective magnetization is observed for (Ga,Mn)Sb, when compared to the other as-grown Ga-Mn-V thin films. This is consistent with

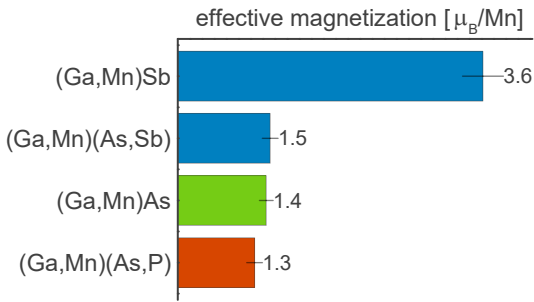


Figure 7.5: Effective magnetization per Mn atom in Ga-Mn-V calculated from SQUID magnetometry data.

low interstitial compensation in the as-grown state of (Ga,Mn)Sb, in contrast with the heavily compensated (Ga,Mn)As systems.

Chapter 8

Local structure of Mn-doped multiferroic GeTe

This chapter explores the rhombohedral distortion, and more specifically the sub-lattice displacement of Mn, on Mn-doped GeTe using the emission channeling technique. It is divided in four sections: first, section 8.1 contextualizes the problematic and focuses on the importance of local structure in the multiferroic properties of (Ge,Mn)Te; second, section 8.2 details on the emission channeling approach to measuring the Mn sub-lattice displacement in GeTe and (Ge,Mn)Te films; third, section 8.3 reports on the results on GeTe films, further assessing the precision obtained in determining the sub-lattice displacement; lastly, section 8.4 reports the results on (Ge,Mn)Te films with varying Mn concentrations, situating them within the multiferroic phase diagram of this material. This chapter concludes with a few remarks on the acquired knowledge about local structure in MUFERS and the challenges and objectives of the field.

8.1 Sub-lattice displacement in multiferroic Rashba semiconductors

As introduced in section 1.3, Mn-doped GeTe experiences a ferroelectric transition at a critical temperature T_C^{FE} . Above T_C^{FE} , it displays a cubic lattice structure, belonging to the $Fm\bar{3}m$ crystallographic space group. The cubic GeTe lattice structure is illustrated in Fig. 8.1(left). Below the transition temperature T_C^{FE} , (Ge,Mn)Te takes on a polar rhombohedral $R\bar{3}m$ phase formed by an elongation of the unit cell along the $\langle 111 \rangle$ direction (cf. Fig. 8.1(right)).^{131,142,229,230} This is caused by a *rhombohedral distortion* which creates a charge imbalance between Ge and Te host atoms, modifying their bond along the $[111]$ axis, and creating a ferroelectric dipole. This fundamental property ultimately confers to α -GeTe, the precursor material from which (Ge,Mn)Te inherits its ferroelectric properties, a ferroelectric polarization.

The rhombohedral distortion is described by two parameters: (i) the angle α between unit vectors $\vec{a}$ and $\vec{c}$, which is 90° in the cubic phase, and $< 90^\circ$ in the rhombohedral phase; and (ii) the sub-lattice displacement Δr of the atom which would otherwise be in the geometric center of the rhombohedral cell, Ge or Mn, illustrated by the arrow in Fig. 8.1(right). Δr is framed in the reference of the Te sub-lattice, and described as the magnitude of a vector from the Ge (or Mn) sub-lattice position towards the Te position along the $\langle 111 \rangle$ direction, as illustrated in Fig. 8.1. This displacement is of the order of $0.30 \text{ \AA}$ for α -GeTe, which corresponds to about 3% of the unit cell diagonal.^{131,142,229,230} A rhombohedral structure is still achievable within the following two situations: (a) if $\alpha < 90^\circ$ and $\Delta r = 0$, and vice-versa (b) if $\alpha = 90^\circ$ and $\Delta r > 0$. In the first case (a), the crystallographic structure is distorted **without** a sub-lattice displacement, which would result in a null ferroelectric polarization and has not been observed in GeTe compounds. The second case (b) also results in a rhombohedral structure, in which there is a displacement between two cubic sub-lattices. This case is expected in (Ge,Mn)Te crystals with Mn contents $x_{\text{Mn}} > 0.30$. Note that both components of the rhombohedral distortion, α and Δr , correspond to small deviations from the perfect cubic structure in GeTe,

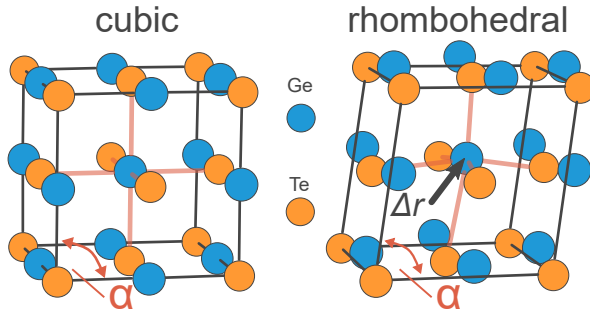


Figure 8.1: Crystallographic structure of ferroelectric Rashba semiconductor GeTe. (left) $Fm\bar{3}m$ rocksalt cubic at temperatures above the ferroelectric T_C^{FE} . (right) $R\bar{3}m$ rhombohedral, below T_C^{FE} . α is the face angle and Δr the sub-lattice displacement along the $[111]$ direction.

and are exaggerated in Fig. 8.1 for illustration purposes.

Introducing Mn dopants in GeTe semiconductors directly influences their structural, ferroelectric and ferromagnetic properties. The solubility of Mn in (Ge,Mn)Te is particularly high, reaching $x_{\text{Mn}} = 0.5$ without impairing the crystalline quality, as confirmed by x-ray diffraction (XRD) and transmission electron microscopy (TEM).^{34,170} This is illustrated in Fig. 8.2, extracted from Ref. 129, showing the rhombohedral distortion, the ferroelectric (FE) and ferromagnetic (FM) transition temperatures as a function of Mn concentration and temperature in (Ge,Mn)Te. The magnitude of the rhombohedral lattice distortion is typically linked with the angle α and with T_C^{FE} , which decrease linearly with Mn concentration, and vanishes at room temperature for $x_{\text{Mn}} > 0.3$ (cf. Fig. 8.2(c)).^{34,129} Additionally, the ferromagnetic T_C^{FM} increases with x_{Mn} , becoming larger than T_C^{FE} at $x_{\text{Mn}} \sim 0.3$.

Coupling between FE polarization and the FM magnetization is mediated by the magnetocrystalline anisotropy associated with the rhombohedral lattice distortion of the FE phase, and, consequently, the sub-lattice displacement Δr . Knowing the magnitude and direction of the sub-lattice displacement Δr becomes then crucial for tuning the interplay between the vertical Zeeman splitting of the bands and the Rashba splitting in the $k_{\parallel}$ direction (cf.

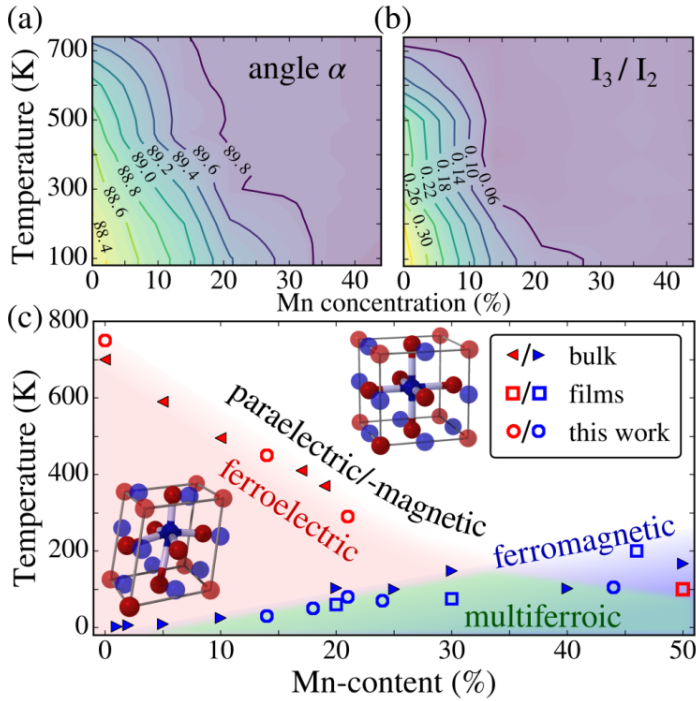


Figure 8.2: Figure and legend extracted from Ref. 129. (a),(b) Contour plots of the unit cell angle α and the I_3/I_2 intensity ratio of the (333) and (222) Bragg peaks that is strongly increased by the anion/cation sub-lattice displacements. (c) Multi-ferroic phase diagram of (Ge,Mn)Te compiled from bulk^{167,231} and thin film^{34,169} data. The blue data points show the FM and the red point the FE phase transition, and the open and closed symbols represent the data from thin films and bulk, respectively. The ferroelectric T_C^{FE} spans from above 700 K to 100 K for x_{Mn} increasing from 0 to 0.5, respectively, and ferromagnetism up to $T_C^{FM} \sim 200$ K at $x_{Mn} = 0.5$. The multiferroic regime where FE and FM coexist is indicated by the green region.

section 1.3.2), which are determined by the relative **FE** polarization and **FM** magnetization directions.^{34, 175, 176}

In (Ge,Mn)Te, the sub-lattice displacement Δr can be independently described for each of the elements which occupy cation positions, i.e. for host Ge and dopant Mn sub-lattices.^{33, 129} Although conventional x-ray diffraction (**XRD**) and x-ray absorption fine structure (**EXAFS**) experiments allow for a reasonable characterization of α and of the magnitude of Δr (at least when Δr is sufficiently large, such as in GeTe), these techniques do not distinguish the direction of $\Delta r(\text{Ge})$ and $\Delta r(\text{Mn})$. In the following sections we will describe how this challenge is approached using the emission channeling technique for determining both the direction and magnitude of the Mn sub-lattice displacement in both GeTe and (Ge,Mn)Te thin films.

8.2 Determining the sub-lattice displacement

Determining the Mn displacement in GeTe and (Ge,Mn)Te films with a sub-Ångström precision challenges the current capabilities of emission channeling, as its resolution is comparable to the sub-lattice displacement in GeTe. Traditionally, emission channeling measures the lattice site of radioactive probes with a precision in the tens of picometers. As an example, Refs. 232, 233 explore the lattice site of ^{24}Na in ZnO and of ^{27}Mg in GaN. In both studies, the radioactive probes were found to occupy two lattice sites, the cation-substitutional site and sites that are displaced from the ideal octahedral interstitial site along the [0001]-axis. This displacement from the ideal octahedral site is of the order of $0.20 - 0.29 \text{ Å}$ for ^{24}Na in ZnO,²³² and of $0.60 \pm 0.14 \text{ Å}$ for ^{27}Mg in GaN.²³³ Both studies point towards a precision in the probes lattice location of the order of 0.1 Å , indicating that the Mn sub-lattice displacement in GeTe and (Ge,Mn)Te is on the limit of emission channeling resolution.

8.2.1 Experimental details

For investigating the local structure and lattice location of Mn in GeTe and (Ge,Mn)Te, β^- emission channeling experiments¹⁸⁰ were performed with radioactive ^{56}Mn (2.56 h) as probes. Following the implantation of the radioactive probes into the crystal, their decay products, in this case β^- particles, are channeled at relativistic speeds along the crystallographic axes and planes. Emitted electrons are diffracted anisotropically, resulting in well-defined channeling or blocking effects, which strongly depend on the initial position of the emitted particles, i.e. the lattice location of the probes in the crystal.

The experiments described here, both on GeTe and (Ge,Mn)Te thin films, were performed at 100 K and at room temperature as a function of Mn concentration, on the on-line setup for emission channeling at ISOLDE, which allows for experiments within the temperature range from 50 K up to 1200 K. Technical details and operation of the setup are not described in this thesis and the reader is referred to Ref. 184 for more information. However, one notable remark to the low-temperature experiments described in the following paragraph relates to the timescale of the experiment compared to the isotopic half-life. The cooling process requires at least two hours to reach 100 K, which can lead to a loss of almost half of the implanted ^{56}Mn activity (half-life of 2.56 h). Additionally, implanting low fluences of ^{56}Mn at room temperature in GeTe and (Ge,Mn)Te is preferred as it minimizes implantation damage. Implanting at lower temperatures increases damage. Consequently, relatively low amounts of radioactivity are available for quantification of the sub-lattice displacement through emission channeling. In order to achieve maximum resolution under these conditions, a careful optimization of the measurement and fitting process was required and is described below.

Table 8.1 lists the various experimental parameters of the emission channeling experiments performed in GeTe and (Ge,Mn)Te films, grown by molecular beam epitaxy (MBE) on BaF_2 substrates at 280°C ,^{129,169,170} except for sample d, which was grown on InP.³³ Implantations of ^{56}Mn probes were performed at room temperature with low fluences in order to minimize damage accumulation with

# _s	year	sample	substrate	Mn %	x_p [cm ⁻³]	R_p [nm]	σ [nm]	fluence [cm ⁻²]
a	2015	GeTe	BaF ₂	0	6.8×10^{17}	33.1	18.7	3.4×10^{12}
b	2016	GeTe	BaF ₂	0	6.4×10^{17}	33.1	18.7	3.2×10^{12}
c	2018	GeTe	BaF ₂	0	4.3×10^{17}	33.1	18.7	2.1×10^{12}
d	2018	GeTe	InP	0	8.1×10^{17}	33.1	18.7	4.0×10^{12}
e	2018	(Ge,Mn)Te	BaF ₂	13	9.4×10^{17}	32.0	18.0	4.7×10^{12}
f	2016	(Ge,Mn)Te	BaF ₂	16	2.8×10^{17}	31.9	17.8	1.3×10^{12}
g	2018	(Ge,Mn)Te	BaF ₂	20	6.7×10^{17}	31.6	17.7	3.2×10^{12}
h	2016	(Ge,Mn)Te	BaF ₂	21	2.9×10^{17}	31.6	17.7	1.4×10^{12}

Table 8.1: Sample and implantation details. All implantations were performed at an angle of $\theta = 17^\circ$ and energy of 50 keV, at room temperature. The peak concentrations x_p , projected ion range (R_p) and straggling (σ) were estimated using the SRIM-2008 code.¹⁹¹

decreasing implantation temperature. Finally, data collection was performed at room temperature and at 100 K, with patterns recorded for both the channeling along $\langle 100 \rangle$ and $\langle 110 \rangle$ directions.

8.2.2 Data analysis

In order to analyze emission channeling experimental data, theoretical β^- emission patterns were calculated for various possible displaced Mn lattice sites using the *manybeam* formalism for electron channeling in single crystals.¹⁸⁰ Quantitative assessment of the ^{56}Mn lattice location was then provided by fitting the two-dimensional experimental patterns with theoretical yield distributions for different lattice sites using a χ^2 -minimization routine.¹⁹² This procedure allows determining the best fitting Mn displacement for each measured pattern, together with a site-fraction associated with each displacement direction, i.e. the amount of ^{56}Mn radioactive probes fitted occupying lattice sites with different displacements. The site fractions were then multiplied by a correction factor which accounts for the contributions of backscattered electrons that reach the detector. This effect was estimated by Geant4 simulations of

electron scattering,^{188,189} which take into account the elemental composition and geometry of the sample, sample holder and vacuum chamber.

8.2.2.1 Assessing the rhombohedral distortion

Assessing the displacement of Mn dopants in GeTe and (Ge,Mn)Te using emission channeling depends both on the nature of the displacement within the rhombohedral distorted structure as well as on the technique's precision and implementation. Here we discuss how emission channeling measurements and *manybeam* simulations were optimized for identifying both the magnitude and direction of displaced Mn lattice sites.

As mentioned previously (section 8.3), there are two parameters that fully characterize the rhombohedral distortion: the angle α and the sub-lattice displacement Δr . Both parameters modify the Coulomb potential acting on the emitted electrons from the radioactive ^{56}Mn decay, along the various crystallographic directions. GeTe and (Ge,Mn)Te thin films were grown along the $\langle 111 \rangle$ direction, presumably the same direction as the rhombohedral distortion and resulting ferroelectric polarization (cf. Fig. 8.1). Accordingly, only by measuring along off-surface directions are we able to quantify the Mn sub-lattice displacement $\Delta r(\text{Mn})$ using emission channeling. This is further illustrated in Fig. 8.5, where the resulting simulated patterns for different sites along the $\langle 111 \rangle$ direction are identical.

Fig. 8.3 shows projected crystallographic lattices for both cubic and rhombohedral phases along three different directions. Each atom represents an atomic row, as seen along the projected directions. The identification of different lattice sites in crystals depends on the nature of the atomic rows projected along different directions. In a cubic crystal the atomic rows as seen along the $\langle 111 \rangle$ and $\langle 100 \rangle$ directions are mixed rows, i.e. the atoms in the row alternate in the z -direction between anion and cation represented in (cf. Fig. 8.3(a,c)). On the contrary, for the $\langle 110 \rangle$ direction the atomic rows are composed of a single element (cf. Fig. 8.3(e)). These typical cubic characteristics are not observed in the rhombohedral phase, even with an angle α very close to 90° , due to the displacement Δr between Ge and Te sub-lattices.

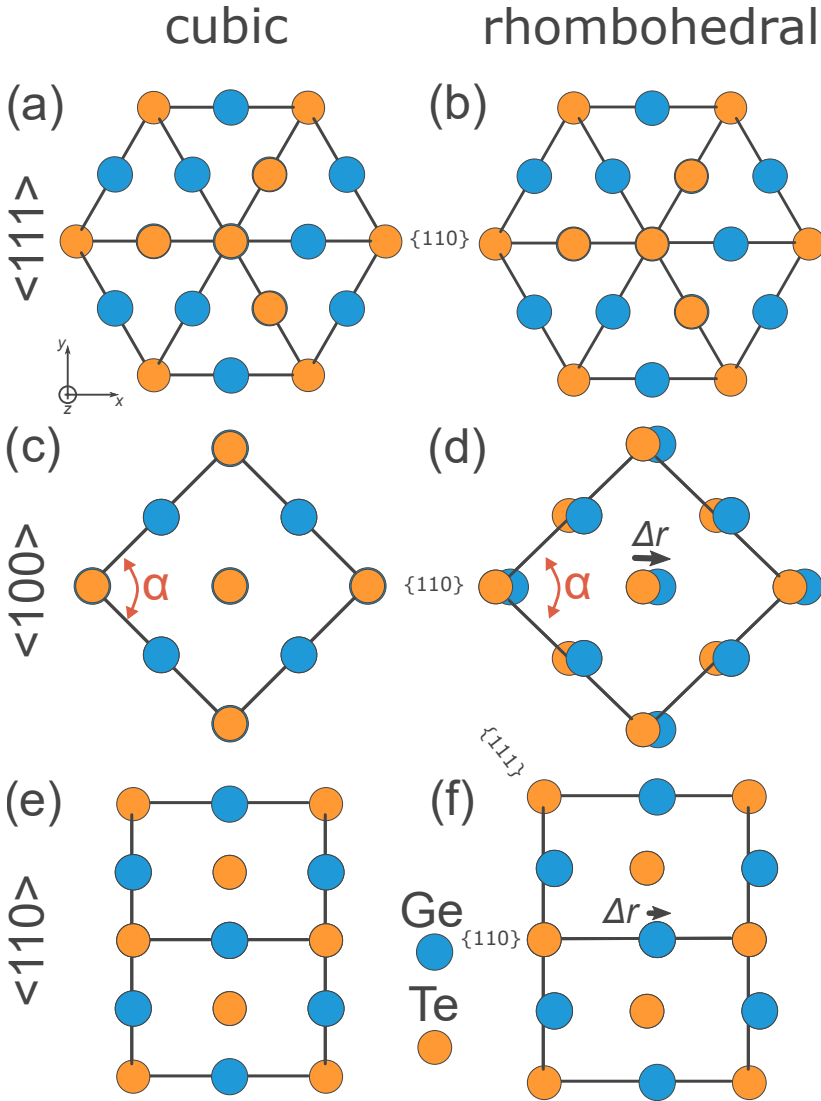


Figure 8.3: Crystallographic projections of the ideal cubic and rhombohedrally distorted lattice structure of GeTe along three main directions: $\langle 111 \rangle$, $\langle 100 \rangle$, and $\langle 110 \rangle$. These projections work as indicators for the Coulomb potential acting on the emitted electrons for each direction. α and Δr are the distortion angle and sub-lattice displacement for GeTe, respectively. The projected Δr is larger for the $\langle 100 \rangle$ direction.

direction	$\theta_{\text{proj}} [^\circ]$	$\Delta r_{\text{proj}} [\text{\AA}]$
$\langle 110 \rangle$	34.0	0.17
$\langle 100 \rangle$	53.5	0.24

Table 8.2: Projected sub-lattice displacement Δr_{proj} for each crystallographic direction assuming $\Delta r(\text{Ge}) = 0.30 \text{ \AA}$. θ_{proj} is the angle between the corresponding direction and the $\langle 111 \rangle$ sub-lattice displacement direction.

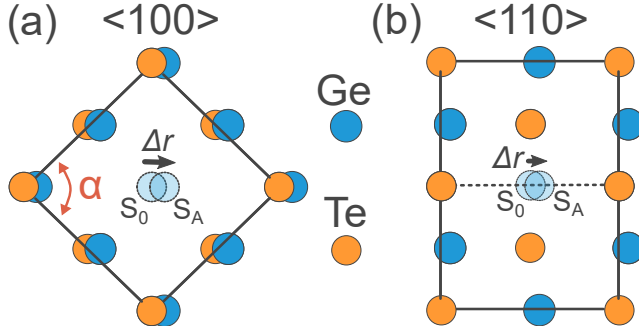


Figure 8.4: Calculated Mn displacement sites in *manybeam* along the (a) $\langle 100 \rangle$ and (b) $\langle 110 \rangle$ directions. Note that the sub-lattice displacement of both Ge and Mn sub-lattices is along the horizontal plane, with orientation defined by the Δr arrows.

Utilizing the literature values for rhombohedral GeTe, $\alpha = 88.2^\circ$ and $\Delta r = 0.30 \text{ \AA}$, Fig. 8.3 shows a clear difference between the projected structures for cubic and rhombohedral cases for the two off-surface directions, $\langle 100 \rangle$ and $\langle 110 \rangle$, a consequence of the breaking of point inversion symmetry in this material. In particular, along the $\langle 100 \rangle$ direction there is a splitting of the mixed atomic row into two single element atomic rows. Assuming a cation-substitutional occupation of the ^{56}Mn probes, this “break-up” of the atomic rows should intuitively have a strong effect on the electron channeling along this direction, effectively modifying the channeling features around the center of the channel. Conversely, measuring along the $\langle 110 \rangle$ should result in a smaller variation on axial channeling features and, possibly, larger effects on the planar channeling, as the atomic rows are displaced proportionally to the projected sub-lattice displacement. Table 8.2 shows projected values for Δr along each off-surface direction in α -GeTe.

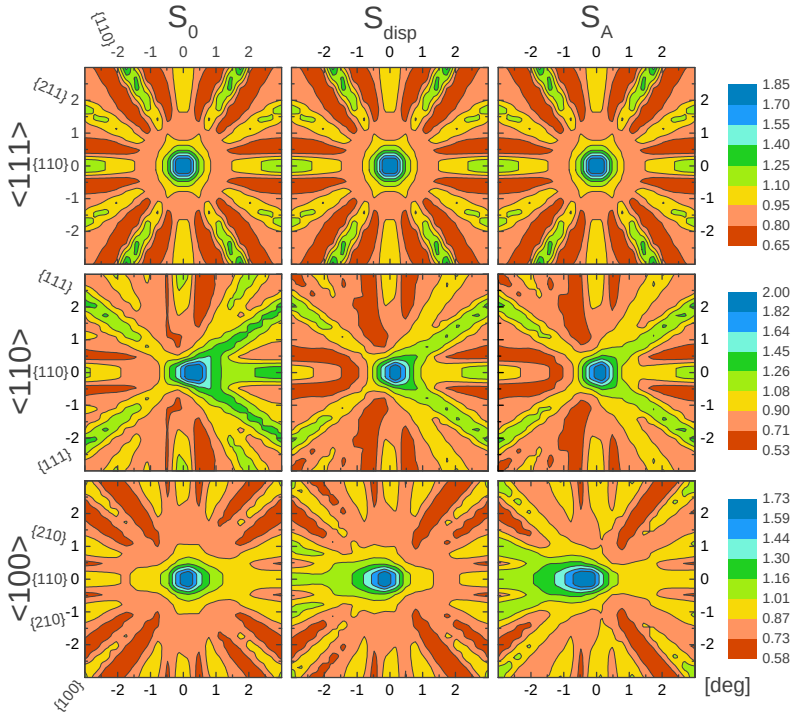


Figure 8.5: Simulated emission channeling patterns, along the $\langle 111 \rangle$, $\langle 110 \rangle$, and $\langle 100 \rangle$ directions, for 100% of emitter atoms (^{56}Mn) on substitutional Ge sites (S_A), average best-fitting displaced sites (S_{disp}), and non-displaced null polarization sites (S_0). S_{disp} and S_A correspond to sub-lattice displacements of 0.20 Å and 0.30 Å, respectively. Left-right asymmetry flips between S_0 and S_A sites along the $\langle 100 \rangle$ direction.

Two essential sites are considered in this analysis: substitutional Mn sites, assumed to be at the same displacements as the Ge sub-lattice and denoted as S_A , and a non-displaced site, corresponding to a site which would yield a null ferroelectric polarization in the crystal, denoted as S_0 . These lattice sites are illustrated in Fig. 8.4 for sub-lattice displacements in accordance with Table 8.2, and act as guidelines for how the sub-lattice displacement could change the electrostatic potential along the two off-surface directions, $\langle 100 \rangle$ and $\langle 110 \rangle$.

Accordingly, *manybeam* simulations were prepared for varying Mn displacements between S_0 and S_A . Fig. 8.5 plots *manybeam* simulations for both S_0 and S_A

lattice sites, together with a third intermediate site S_{disp} , correspondent to the best fit displacement obtained from the analysis of the ^{56}Mn experiment in GeTe films, described in section 8.3. In this figure the stark difference between S_0 and S_A sites for $\langle 100 \rangle$ and $\langle 110 \rangle$ patterns becomes evident: while varying between these sites results in minor visual changes in atomic and planar channeling features between $\langle 110 \rangle$ patterns, for $\langle 100 \rangle$ patterns there is a “flip” in left-right asymmetry. Together with a larger projected Δr along the $\langle 100 \rangle$, this effect hints at a higher precision for determining the sub-lattice displacement for measurements along this direction when compared to $\langle 110 \rangle$. Other sites were also simulated, considering displacements along the $\langle 111 \rangle$ direction less than S_0 and beyond S_A , trending towards interstitial sites.

Interstitial sites were not considered for these experiments for a few fundamental and computational reasons. First, there are no interstitial sites in the cubic rocksalt structure with similar symmetry to substitutional sites, like the tetrahedral interstitial site in *zincblende* structures (cf. 4), which is usually a prerequisite for interstitial impurity formation. This is further reinforced by the lack of theoretical predictions or experimental observations of interstitial sites in literature for GeTe and (Ge,Mn)Te crystals. Second, magnetometry measurements in (Ge,Mn)Te films report a magnetization consistent with fully substitutional incorporation.^{34,169} Finally, the uncertainty on the Ge and Mn sub-lattice displacement in (Ge,Mn)Te films would probably add up to inaccurate channeling contributions in interstitial sites, besides dramatically increasing *manybeam* computing time.

The crystalline details described up to now point towards the $\langle 100 \rangle$ as the optimal measuring direction in which to optimize emission channeling sensitivity to the **magnitude** of $\Delta r(\text{Mn})$. Gathering insight on the displacement **direction** requires an additional analysis of the fitting of emission channeling experiments to *manybeam* simulations. Assuming a perfect single crystal epitaxy, characteristic of **LT-MBE**-grown crystals, the rhombohedral distortion in GeTe and (Ge,Mn)Te has been observed to mostly follow the growth $[111]$ direction, with only about 10% of the volume accounting for crystalline domains oriented towards other tilted $[111]$ directions (for Mn concentrations up to 20% in Mn-doped GeTe).¹²⁹ Furthermore, as detailed in section 1.3.1, the **FE**

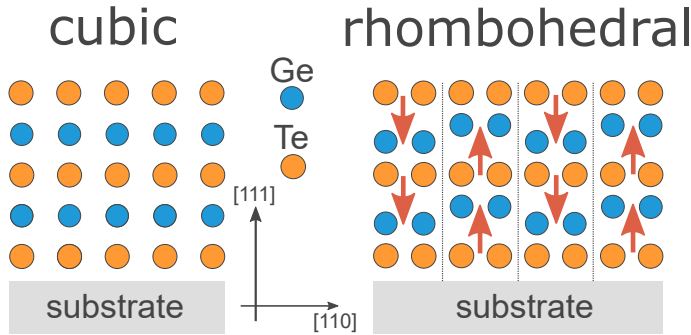


Figure 8.6: Illustration of a GeTe $\langle 110 \rangle$ crystalline cross-section. Below the [FE](#) transition temperature and in the as-grown state, without previous application of electric fields, the sub-lattice displacement can vary between different crystalline domains.

polarization in GeTe crystals is associated with the direction of the rhombohedral distortion and the cation/anion sub-lattice displacement. Consequently, different crystallographic grains align along the $[111]$ direction, resulting from thin film growth, and have two possibilities for the orientation of the Ge (or Mn) sub-lattice displacement: out-of-surface or towards-surface, i.e. $\langle 111 \rangle$ or $\langle \bar{1}\bar{1}\bar{1} \rangle$. This is further illustrated in Fig. 8.6, where both orientations of crystalline domains are shown.

In this context, we turn to the nature of emission channeling when probing an epitaxial film with differently oriented crystalline domains. Emission channeling makes use of the implantation of radioactive ^{56}Mn isotopes into the target GeTe or (Ge,Mn)Te samples, observing the resulting channeling of emitted β^- electrons using a position sensitive detector. While the experimental setup and implantation parameters are all taken into consideration during the analysis and fitting procedure, the macroscopic crystalline nature of the sample can still influence the experimental results. In other words, the implanted region, or *beamspot*, although limited to the surface area of a 1 mm diameter circle,¹⁸⁴ may enclose several crystalline domains and, consequently, the technique will probe domains with opposing sub-lattice displacements. In order to account for this effect, the analysis of emission channeling data requires the simultaneous fitting of *manybeam* simulations allowing for sub-lattice displacements in both

orientations of the $[111]$ axis. More specifically, the fitting procedure is allowed to simultaneously fit two theoretical patterns with the same Δ_r that are azimuthally rotated 180° with respect to each other. Therefore, it is possible to determine the fractions of ^{56}Mn probes occupying displacements along each orientation (pointing out-of-surface or toward the surface).

Finally, following the guidelines provided in this section, sets of *manybeam* simulations were prepared for GeTe and (Ge,Mn)Te at different concentrations (cf. Table 8.1). The following sections detail on the results of both sets of experiments: first focusing on the the precision of emission channeling in determining the lattice location of ^{56}Mn in GeTe films (i.e. not doped with Mn during growth), and then extending to (Ge,Mn)Te thin films doped with Mn during growth.

8.3 Mn lattice location in α -GeTe

In order to precisely determine the ^{56}Mn lattice location in GeTe and (Ge,Mn)Te films using the emission channeling technique a few sources of error are considered: experimental error, statistical error and fit error. For this purpose, several emission channeling experiments were performed in GeTe thin films at a few selected temperatures, i.e. 100 K, 298 K and 398 K.

Fig. 8.7 shows normalized β^- experimental patterns and corresponding best fits in the vicinity of $\langle 100 \rangle$ and $\langle 110 \rangle$ directions at 100 K in sample (c), GeTe on InP in Table 8.1. There is an evident mismatch between experimental and best fit patterns, particularly for the planar channeling features. This mismatch can be caused either by experimental errors and/or errors in the theoretical model utilized for analysis. On the one hand, there are multiple sources of experimental error which can reduce the quality of an emission channeling experiment: unaccounted for background radiation, irregular beam spot, sample mosaicity, implantation of different radioactive elements with the same mass. On the other hand, the theoretical model utilized to produce *manybeam* simulations may also introduce errors in the fitting procedure through a flawed implementation of the crystallographic structure, different implanted

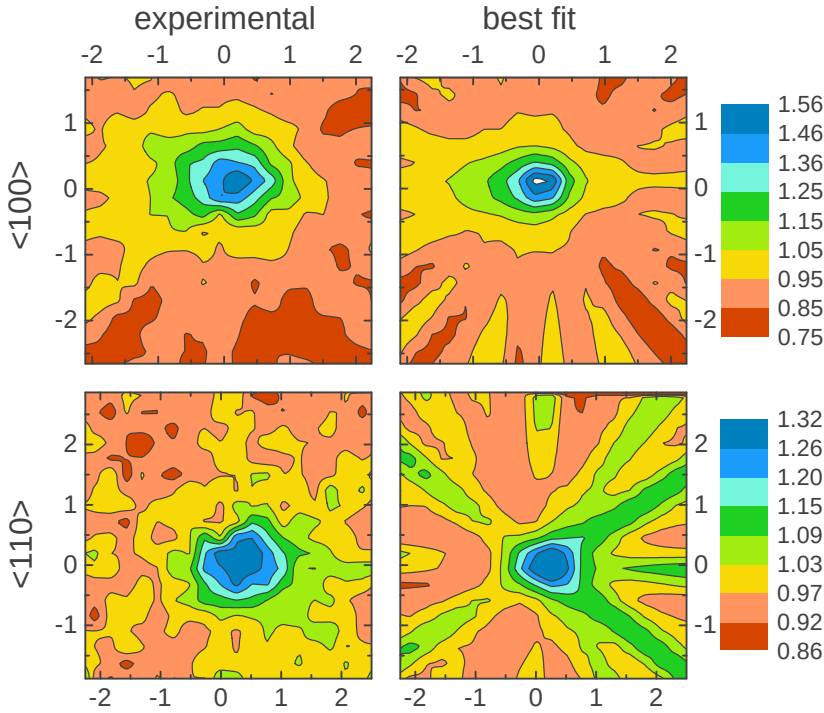


Figure 8.7: (a)-(b) Normalized experimental β^- emission channeling patterns in the vicinity of $\langle 100 \rangle$ and $\langle 110 \rangle$ directions in GeTe at 100 K, and corresponding best fits (c)-(d).

probe depth profiles, or even dechanneling by heavier elements, which is less well defined than for light elements. Among these different sources, two stand-out as likely candidates to justify the mismatch between experimental and best fit patterns: sample mosaicity on the experimental error side, and incorrect crystallographic structure model on the theoretical one. While the latter can in principle be excluded, the former can explain the observed mismatch. Mosaicity is a measure of the spread of crystal plane orientations and it has been observed to lead to a broadening of planar channeling effects, possibly reducing fitted fractions, particularly in off-surface directions.¹⁸⁶ These effects are consistent with the mismatch in Fig. 8.7. Mosaicity has not yet been investigated in the GeTe and (Ge,Mn)Te films and its effect cannot be immediately estimated for

# _e	# _s	direction	substrate	T [K]	$\Delta r(\text{Ge})$ [Å]	$\Delta r(^{56}\text{Mn})$ [Å]	$f_{\langle 111 \rangle}$	$f_{\langle \bar{1}\bar{1}\bar{1} \rangle}$
i	c	$\langle 100 \rangle$	BaF ₂	100	0.3	0.17	1.00	0.01
ii	c	$\langle 100 \rangle$	BaF ₂	298	0.3	0.17	0.95	0.05
iii	d	$\langle 100 \rangle$	InP	100	0.3	0.17	0.77	0.01
iv	d	$\langle 100 \rangle$	InP	298	0.3	0.21	0.57	0.42
v	b	$\langle 100 \rangle$	BaF ₂	398	0.3	0.18	0.77	0.22
vi	a	$\langle 100 \rangle$	BaF ₂	298	0.3	0.24	0.61	0.37
vii	c	$\langle 110 \rangle$	BaF ₂	100	0.3	0.24	0.71	0.13
viii	c	$\langle 110 \rangle$	BaF ₂	298	0.3	0.36	0.62	0.25
ix	d	$\langle 110 \rangle$	InP	100	0.3	0.17	0.38	0.01
x	d	$\langle 110 \rangle$	InP	298	0.3	0.39	0.41	0.13
xi	b	$\langle 110 \rangle$	BaF ₂	398	0.3	0.24	0.63	0.01
xii	a	$\langle 110 \rangle$	BaF ₂	298	0.3	0.21	0.60	0.04

Table 8.3: Best fit parameters for $\Delta r(^{56}\text{Mn})$ for ^{56}Mn emission channeling experiments in GeTe films performed along the $\langle 100 \rangle$ (a-f) or $\langle 110 \rangle$ (g-l) directions. #_e us the experiment number and #_s the sample identification from Table 8.1. $\Delta r(\text{Ge})$ is the Ge sub-lattice displacement implemented in *manybeam* simulations. $f_{\langle 111 \rangle}$ and $f_{\langle \bar{1}\bar{1}\bar{1} \rangle}$ correspond to fitted fractions of ^{56}Mn displacement associated with either out-of-surface or towards-surface orientation.

our emission channeling experiments. However, based on Ref. 186, we expect a more significant effect on the fitted fractions than on the lattice location of ^{56}Mn probes, i.e. without significantly affecting our main findings.

Table 8.3 summarizes all the experimental results and the fit parameters for the emission channeling experiments, emphasizing the ^{56}Mn sub-lattice displacement $\Delta r(\text{Mn})$ and the two corresponding fitted-fractions for displacements along the $\langle 111 \rangle$ direction: $f_{\langle 111 \rangle}$ and $f_{\langle \bar{1}\bar{1}\bar{1} \rangle}$. Averaging the best fits for all samples per direction yields a $\Delta r(^{56}\text{Mn})$ of 0.19 ± 0.02 Å for measurements along the $\langle 100 \rangle$ direction, and 0.26 ± 0.04 Å for $\langle 110 \rangle$. The smaller experimental spread in Δr for measurements along the $\langle 100 \rangle$ direction than $\langle 110 \rangle$ is in line with our expectation that the $\langle 100 \rangle$ direction is best suited to measure Δr , as discussed in section 8.2. These results can be further refined by taking into account that experiments performed at higher temperatures should result in a less precise

lattice location, due to larger average thermal displacement of both host atoms and ^{56}Mn probes. Hence, excluding the results from experiments performed at 298 K and 398 K, we obtain an average $\Delta r(^{56}\text{Mn}) = 0.17 \pm 0.01 \text{ \AA}^{\text{a}}$ for measurements along the $\langle 100 \rangle$ direction, and $\Delta r(^{56}\text{Mn}) = 0.20 \pm 0.02 \text{ \AA}$ for $\langle 110 \rangle$.

Figure 8.8 shows reduced χ^2 curves obtained from fitting emission channeling experiments on GeTe films along $\langle 100 \rangle$ and $\langle 110 \rangle$ directions with *manybeam* simulations for various displaced Mn lattice sites along the $[111]$ axis and in the vicinity of the Ge-substitutional site. The statistical error for the fits presented in Table 8.3 and plotted in Fig. 8.8 was estimated to be smaller than $0.005 \text{ \AA}$, i.e. smaller than the symbol size. This is a consequence of the high statistics of emission channeling patterns, where each pixel in the detector records a large number of events N , driving the fit error by $1/\sqrt{N}$.

In accordance with the experimental and best fit patterns displayed in Fig. 8.7, these results also show stark differences between reduced χ^2 curves corresponding to $\langle 100 \rangle$ and $\langle 110 \rangle$ measurements. These differences are related with a combination of the simultaneous fitting of oppositely oriented patterns and with the “break-up” of mixed atomic rows into two single atomic rows in $\langle 100 \rangle$ measurements (cf. section 8.2). Additionally, albeit the fitting procedure yields a larger uncertainty and (possibly) error in best fit $\Delta r(^{56}\text{Mn})$ for patterns measured along the $\langle 110 \rangle$ direction, these measurements are essential for the interpretation of $\langle 100 \rangle$ fits. More information on these details and on this analysis procedure can be found in section 8.3.2.

Fig. 8.9 plots the best fitting $\Delta r(^{56}\text{Mn})$ for every experiment and their average as a function of measuring direction. Despite the different experimental parameters (different samples and temperatures), measuring along the $\langle 100 \rangle$ direction clearly yields a smaller experimental spread in best fitting $\Delta r(^{56}\text{Mn})$ than along the $\langle 110 \rangle$ direction. This experimental spread is illustrated by the error bar in displacement in gray in the figure.

Finally, the displacement of ^{56}Mn in GeTe films can be estimated by weighting

^aSame best fit displacement for both low temperature measurements along the $\langle 100 \rangle$ direction. Accordingly the uncertainty is given by the fit error which is lower than $0.005 \text{ \AA}$.

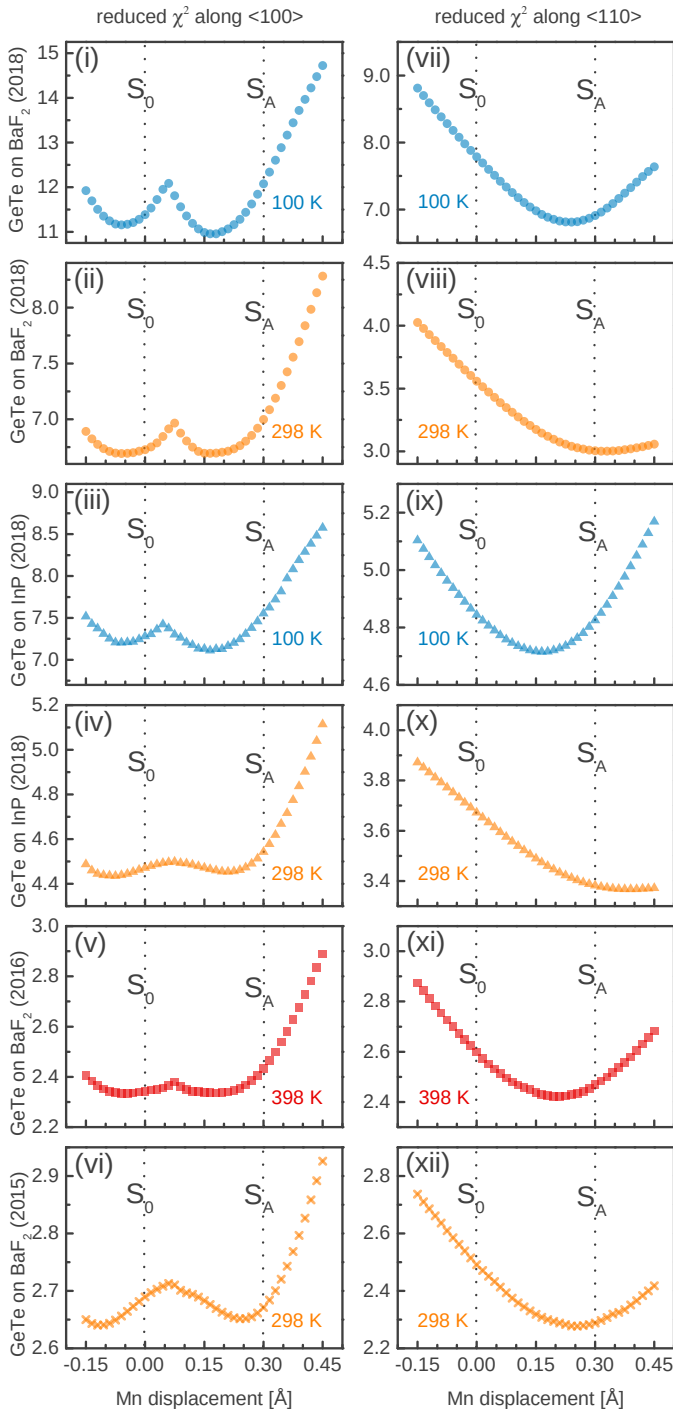


Figure 8.8: Reduced χ^2 curves of fitted experimental patterns acquired the $\langle 100 \rangle$ and $\langle 110 \rangle$ directions in GeTe films, to *manybeam* simulations for various Mn displacements along the $[111]$ axis. S_0 and S_A represent the ideal substitutional and the Ge-substitutional sites, respectively.

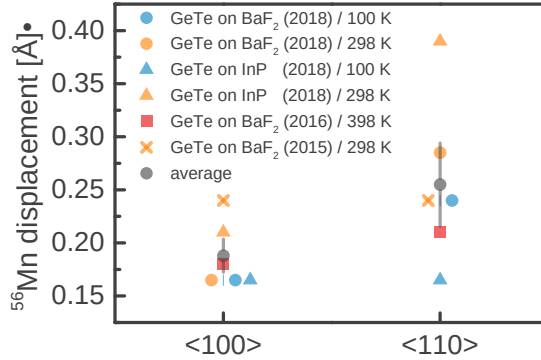


Figure 8.9: Best fitting ^{56}Mn displacement for every experiment for each measuring direction, $\langle 100 \rangle$ and $\langle 110 \rangle$. A smaller average and standard deviation is observed for data measured along the former direction, indicating a higher precision in the $\Delta r(^{56}\text{Mn})$ determination using emission channeling.

low temperature			all temperatures		
direction	$\overline{\Delta r}$ [Å]	$\sigma(\Delta r)$ [Å]	direction	$\overline{\Delta r}$ [Å]	$\sigma(\Delta r)$ [Å]
$\langle 100 \rangle$	0.17	0.01 ^b	$\langle 100 \rangle$	0.19	0.03
$\langle 110 \rangle$	0.20	0.05	$\langle 110 \rangle$	0.26	0.08
$\langle 100 \rangle \& \langle 110 \rangle$	0.19		$\langle 100 \rangle \& \langle 110 \rangle$	0.22	
$\sigma(\langle 100 \rangle \& \langle 110 \rangle)$	0.03		$\sigma(\langle 100 \rangle \& \langle 110 \rangle)$	0.05	

Table 8.4: Average ($\overline{\Delta r}$) and standard deviation ($\sigma(\Delta r)$) between best fit results of all experiments per measuring direction. On the left, values considering only low temperature experiments, on the right, all experiments. Average and standard deviation between directions is also provided for each set.

the possible sources of error discussed above. Regarding experimental errors, both experimental and analysis procedures were developed in order to minimize their impact on the results. Despite the possibility for sample mosaicity in some GeTe films, experimental errors do not seem to hinder a quantitative determination of the ^{56}Mn lattice displacement, as illustrated by the small spread in best fit results in Fig. 8.9 and present in Table 8.4. Fit errors can also be safely neglected due to the large amount of events characteristic of emission channeling experiments, as described above. Consequently, in the present analysis the most dominant uncertainty source comes from statistical

errors. Table 8.4 shows averages and standard deviations of best fit results for all measurements for two statistical sets: only low temperature measurements, and all measurements. As mentioned previously, measuring at lower temperatures should yield a more precise ^{56}Mn lattice location due to lower average thermal displacements, illustrated by the small standard deviation between $\langle 100 \rangle$ and $\langle 110 \rangle$ results at this temperature. On the other hand, assessing only $\langle 100 \rangle$ measurements for all temperatures yields very similar results. Since the displacement of both Ge and Mn sub-lattices is not expected to vary greatly with temperature,^{129,140,234} a conservative estimate for the precision can be extracted from the experimental spread at low temperatures, i.e. $\delta(\Delta r(^{56}\text{Mn})) = 0.03 \text{ \AA}$ (cf. Table 8.4). Additionally, the results presented here for GeTe indicate that measurements along the $\langle 100 \rangle$ provide higher precision in the estimation of the ^{56}Mn lattice location both in GeTe and (Ge,Mn)Te films. Therefore, in section 8.4, the analysis of (Ge,Mn)Te films will focus on $\langle 100 \rangle$ measurements, and the error bar will be taken as $\delta(\Delta r(^{56}\text{Mn})) = 0.03 \text{ \AA}$.

8.3.1 Sensitivity to Ge sub-lattice displacement

As described in section 8.2.2.1, crystallites in GeTe films grown by LT-MBE display a preferential orientation along the surface $[111]$ axis, with only a small percentage oriented along the other $[111]$ axes. Additionally, the Ge sub-lattice displacement can follow either orientation along the growth direction, i.e. out-of-surface $\langle 111 \rangle$ or towards-surface $\langle \bar{1}\bar{1}\bar{1} \rangle$. Different $[111]$ -oriented crystallites can then have sub-lattice displacements oriented in either orientation, and the overall population of each orientation may depend mostly on the substrate as well as on growth conditions.

Using the emission channeling technique we were able to probe the orientation of the ^{56}Mn lattice location distortion, which might be intimately connected with the Ge sub-lattice displacement orientation. In the experiments presented here, we observed that there is a predominant fraction of ^{56}Mn probes occupying displaced sites with a $\langle 111 \rangle$ out-of-surface orientation. Fig. 8.10 plots the fractions corresponding to the best fits in Table 8.3 for all experiments as a function of the displacement direction, $\langle 111 \rangle$ or $\langle \bar{1}\bar{1}\bar{1} \rangle$. Moreover, the fact

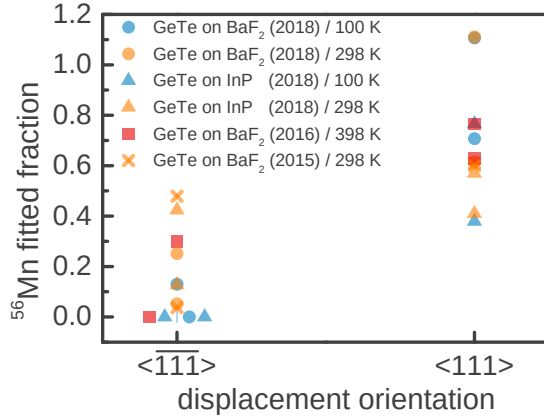


Figure 8.10: ^{56}Mn best fitting fractions along and against the growth $[111]$ direction. There is an asymmetry in $\Delta r(^{56}\text{Mn})$ fractions, possibly pointing towards a spontaneous **FE** polarization of GeTe.

#	direction	T [K]	$\Delta r(\text{Ge})$ [Å]	$\Delta r(^{56}\text{Mn})$ [Å]	$f_{\langle 111 \rangle}$	$f_{\langle \bar{1}\bar{1}\bar{1} \rangle}$
i	$\langle 100 \rangle$	100	0.27	0.18	1.07	0.11
ii	$\langle 100 \rangle$	100	0.30	0.17	1.00	0.01
iii	$\langle 100 \rangle$	100	0.33	0.17	1.15	0.01
iv	$\langle 110 \rangle$	100	0.27	0.15	0.75	0.01
v	$\langle 110 \rangle$	100	0.30	0.20	0.73	0.04
vi	$\langle 110 \rangle$	100	0.33	0.25	0.72	0.08

Table 8.5: Best fitting $\Delta r(^{56}\text{Mn})$ for EC experiments performed in 2018 along the $\langle 100 \rangle$ (i-iii) or $\langle 110 \rangle$ (iv-vi) directions for GeTe on BaF_2 substrates. $\Delta r(\text{Ge})$ is the host sub-lattice displacement implemented in *manybeam* simulations; $f_{\langle 111 \rangle}$ and $f_{\langle \bar{1}\bar{1}\bar{1} \rangle}$ correspond to fitted fractions of ^{56}Mn displacement associated with either out-of-surface or towards-surface orientation.

that a preferential orientation is observed indicates a possible spontaneous **FE** polarization along $\langle 111 \rangle$.

In order to test if the magnitude of the sub-lattice displacement of the host ($\Delta r(\text{Ge})$, used as an input in our *manybeam* simulations) had an effect on the value determined for ^{56}Mn from our data, *manybeam* simulations were performed for varying $\Delta r(\text{Ge})$, 0.27 Å, 0.30 Å, and 0.33 Å. Best fit results for

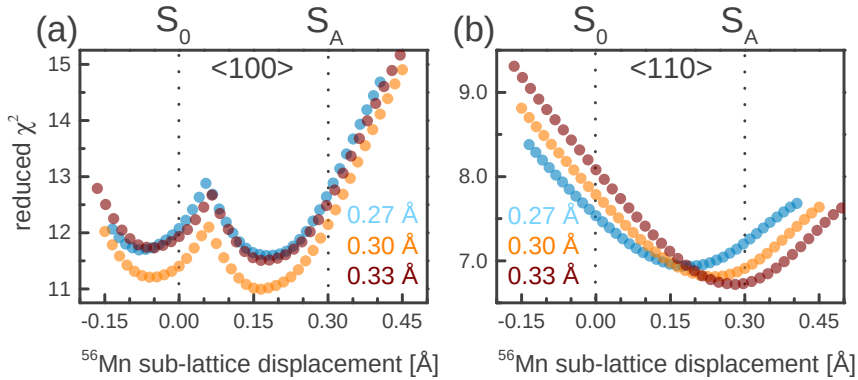


Figure 8.11: Reduced χ^2 of the fits to the experimental $\langle 100 \rangle$ and $\langle 110 \rangle$ patterns of GeTe at 100 K as a function of ^{56}Mn displacement along the $[111]$ axis. Three sets of *manybeam* simulations were utilized, with varying Ge sub-lattice displacement, $\Delta r(\text{Ge})$, 0.27 Å, 0.30 Å, and 0.33 Å.

$\langle 100 \rangle$ and $\langle 110 \rangle$ GeTe patterns measured at 100 K are presented in table 8.5. Reduced χ^2 curves of the fits as a function of ^{56}Mn displacement along the $[111]$ axis are presented in Fig. 8.11. We observe that the best fit result for the ^{56}Mn displacement $\Delta r(\text{Mn})$ obtained from the analysis of $\langle 100 \rangle$ patterns has a negligible dependence on the choice of $\Delta r(\text{Ge})$. The $\langle 110 \rangle$ fits either show a stronger dependence on the $\Delta r(\text{Ge})$ input value, or show poor precision for ^{56}Mn altogether. This further supports the choice of the $\langle 100 \rangle$ axis to measure $\Delta r(\text{Mn})$. The best fit is obtained for a host sub-lattice displacement $\Delta r(\text{Ge})$ of 0.30 Å, in agreement with what has been determined using EXAFS.^{129,140,234} The fact that varying the input $\Delta r(\text{Ge})$ by 0.06 Å has no significant effect on the measured $\Delta r(^{56}\text{Mn})$ is particularly relevant in section 8.4, dedicated to (Ge,Mn)Te films doped during growth, for which the $\Delta r(\text{Ge})$ is less well-defined.

8.3.2 Reduced χ^2 analysis: $\langle 100 \rangle$ versus $\langle 110 \rangle$

The reduced χ^2 curves for $\langle 100 \rangle$ and $\langle 110 \rangle$ fits show significant differences, with two possible best-fitting minima for the former and only one for the latter case (Figs. 8.8 and 8.11). We can understand this difference if we consider two aspects: (i) the splitting of the mixed atomic rows into two single occupancy

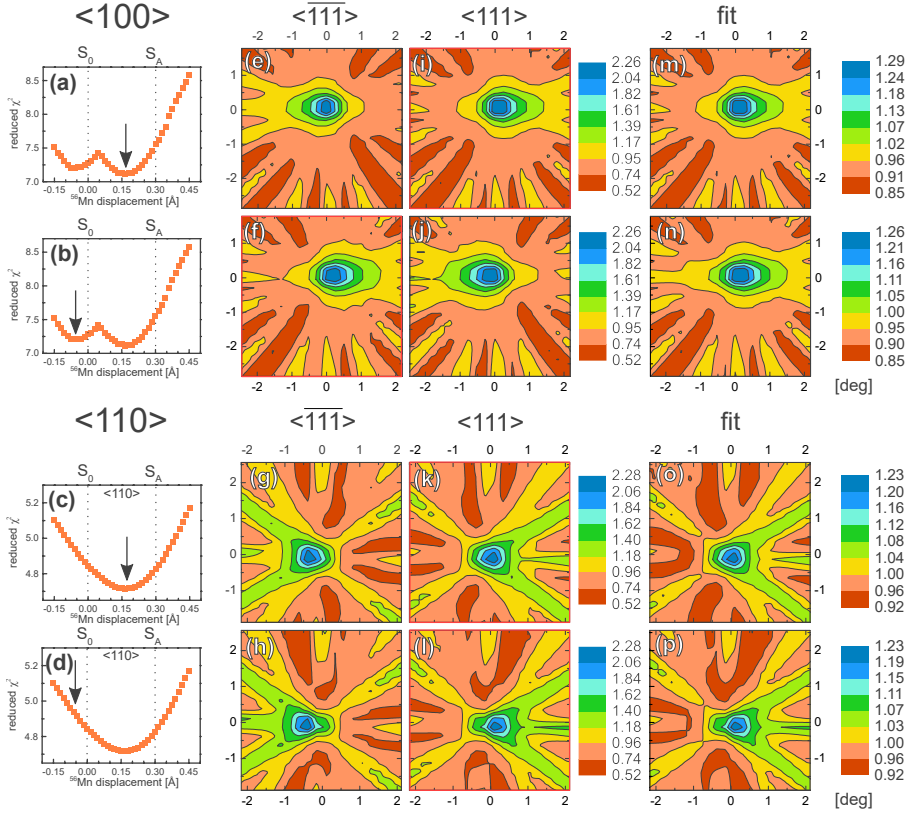


Figure 8.12: (a)-(d) Reduced χ^2 curves of the fits to the experimental $\langle 100 \rangle$ (a-b) and $\langle 110 \rangle$ (c-d) patterns of GeTe on InP at 100 K as a function of ^{56}Mn displacement along the $[111]$ axis. The gray arrows indicate the $\Delta r(^{56}\text{Mn})$ correspondent to the patterns on the right; (e)-(l) normalized simulated $\langle 100 \rangle$ and $\langle 110 \rangle$ patterns for a Ge sub-lattice displacement along the $\langle \bar{1}\bar{1}\bar{1} \rangle$ orientation (e-h) and along the $\langle 111 \rangle$ (i-l); (m)-(p) normalized β^- patterns illustrating the fit between both simulated patterns on the left at $\Delta r(^{56}\text{Mn})$.

rows, and (ii) the fact that we allow the fit to include displacements in both opposite orientations (with the same magnitude of $\Delta r(^{56}\text{Mn})$ to minimize the amount of fitting parameters), i.e. domains polarized antiparallel to each other.

Starting with (i), the small splitting between Ge and Te atomic rows along the $\langle 100 \rangle$ direction strongly influences the channeling features of electrons emitted from ^{56}Mn occupying sites between S_0 and S_A , as described in section 8.2. For the case of the $\langle 100 \rangle$ patterns, this split between single element rows – which is no more than the projected Ge sub-lattice displacement – is smaller than the probed ^{56}Mn displacement range. Consequently, within this range we observe a left-right mirroring of channeling features. On the other hand, for $\langle 110 \rangle$ patterns the split between Ge and Te atom rows is larger, and the sub-lattice displacement only slightly displaces the Ge host lattice. No mirroring of channeling features is observed. This effect is illustrated in Fig. 8.12(e-l), where we plot simulated patterns with differently oriented Ge sub-lattice displacements for $\langle 100 \rangle$ and $\langle 110 \rangle$ directions.

The second (ii) effect is related to the simultaneous fit of simulated patterns with opposite Ge sub-lattice displacement orientations to the experimental data. This effect is the one responsible for the observation of a *double-minimum* in $\langle 100 \rangle$ χ^2 curves, as well as for its absence in $\langle 110 \rangle$ curves. Because the distance between Ge and Te atom rows is significantly larger when probing along $\langle 110 \rangle$, the simultaneous fit of both orientations does not overlap the effect described in (i), resulting in only one minimum in the reduced χ^2 curve. Moreover, the opposite is true for the $\langle 100 \rangle$ fits. This is clearly illustrated when comparing the fits for each local minimum, i.e. $\Delta r(^{56}\text{Mn})$ for each orientation within each measuring direction, represented in Fig. 8.12. By visual inspection, fit (m) and (n) are virtually the same, whilst corresponding to different $\Delta r(^{56}\text{Mn})$. Additionally, fit (m) is similar to simulation (i), while fit (n) is similar to simulation (f). Simulations (f) and (i) correspond to opposing orientations, but $\Delta r(^{56}\text{Mn})$ are also opposed in sign. Accordingly, there are two consequences: (1) ^{56}Mn lattice location experiments using $\langle 100 \rangle$ patterns yield ambiguous results regarding the Ge sub-lattice displacement; and (2) $\langle 110 \rangle$ reduced χ^2 curves are required to determine the best fit in $\langle 100 \rangle$ χ^2 curves. Although $\langle 110 \rangle$ χ^2 curves produce less “sharp” minima with a larger displacement uncertainty, their fits

do not display the contradiction observed for $\langle 100 \rangle$ measurements. This is illustrated by the good visual agreement between fits (o)-(p) with simulations (k)-(l), respectively.

In short, $\langle 100 \rangle$ patterns provide higher precision in ^{56}Mn lattice location, but are ambiguous with respect to two possible best-fit values; the $\langle 110 \rangle$ patterns solve this ambiguity.

8.3.3 Summary

In summary, there are four main observations from our ^{56}Mn emission channeling experiments in α -GeTe films. First, the ^{56}Mn probes occupy displaced substitutional sites in GeTe films, at a displacement of $\Delta r(^{56}\text{Mn}) = 0.19 \pm 0.03 \text{ \AA}$ along the $[111]$ axis. Additionally, while this displacement has not been measured or calculated in literature in the ultra-dilute regime ($< 0.05\%$ Mn), it follows the trend of the data in Ref. 129, where $\Delta r(^{56}\text{Mn})$ is smaller than the host's $\Delta r(\text{Ge}) = 0.30 \text{ \AA}$. Second, the precision depends on the channeling direction: it is higher for $\langle 100 \rangle$ than for $\langle 110 \rangle$. As a conservative limit for the precision with which we can determine the ^{56}Mn lattice location based on $\langle 100 \rangle$ patterns, we take $\sigma(\Delta r) = 0.03 \text{ \AA}$. Third, the best-fitting ^{56}Mn displaced site seems to be largely independent of the Ge displacement used as input in the simulations. Fitting the experimental data with simulated patterns where $\Delta r(\text{Ge})$ was varied, within a $0.27 - 0.33 \text{ \AA}$ range, yields the same position for ^{56}Mn within error. Finally, within the probed region, the ^{56}Mn displacement was observed to lie preferentially along the $\langle 111 \rangle$ direction instead of $\langle \overline{1}\overline{1}\overline{1} \rangle$, i.e. in out-of-surface orientation. Assuming there is a coupling between the Ge sub-lattice displacement and ^{56}Mn lattice site, this suggests that there is spontaneous FE polarization of GeTe in the as-grown state. Although it is not possible to identify the origin of this spontaneous polarization based on our data, it is likely related to the broken inversion symmetry at the film surface or interface.

# _s	Mn %	method	$\Delta r(\text{Ge})$ [Å]	$\Delta r(^{56}\text{Mn})$ [Å]	$f_{\langle 111 \rangle}$	$f_{\langle \bar{1}\bar{1}\bar{1} \rangle}$
c	0	DFT	0.30	0.17	1.00	0.01
e	13	DFT	0.23	0.16	0.76	0.19
f	16	DFT	0.21	0.17	0.53	0.42
g	20	DFT	0.20	0.14	0.80	0.06
h	21	DFT	0.20	0.14	0.28	0.01
c	0	EXAFS	0.30	0.17	1.00	0.01
e	13	EXAFS	0.28	0.17	0.77	0.16
f	16	EXAFS	0.27	0.18	0.54	0.41
g	20	EXAFS	0.23	0.14	0.84	0.01
h	21	EXAFS	0.23	0.14	0.28	0.01

Table 8.6: (Ge,Mn)Te samples, their structural parameters used during analysis and corresponding best fit results. $\Delta r(^{56}\text{Mn})$ is the best fit displacement at 100 K, for $\langle 100 \rangle$ patterns as a function of Mn concentration and simulated $\Delta r(\text{Ge})$. Different values for $\Delta r(\text{Ge})$ reflect *manybeam* simulations using DFT and EXAFS results extracted from Ref. 129. $f_{\langle 111 \rangle}$ and $f_{\langle \bar{1}\bar{1}\bar{1} \rangle}$ correspond to fitted fractions of ^{56}Mn displacement associated with either out-of-surface or towards-surface orientation.

8.4 Mn lattice location in (Ge,Mn)Te

This section builds on the previous one dedicated to ^{56}Mn in rhombohedral GeTe films, extending it to (Ge,Mn)Te thin films doped during growth. For this purpose, emission channeling experiments were performed in (Ge,Mn)Te films as a function of Mn concentration up to 21%, measured at a temperature of 100 K. Based on the reported phase diagram (cf. Fig. 8.2(c)), our (Ge,Mn)Te films are in principle in a ferroelectric phase at 100 K for Mn concentrations up to $\sim 20\%$. In addition, while the samples with the highest Mn content (20% and 21%) are close to the FM transition at this temperature in the phase diagram in Fig. 8.2(c), our measurements are most likely performed above the FM transition, considering the disorder introduced by the ^{56}Mn implantation, which can effectively lower both T_C^{FE} and T_C^{FM} .

Figure 8.13 shows normalized β^- experimental patterns and corresponding best

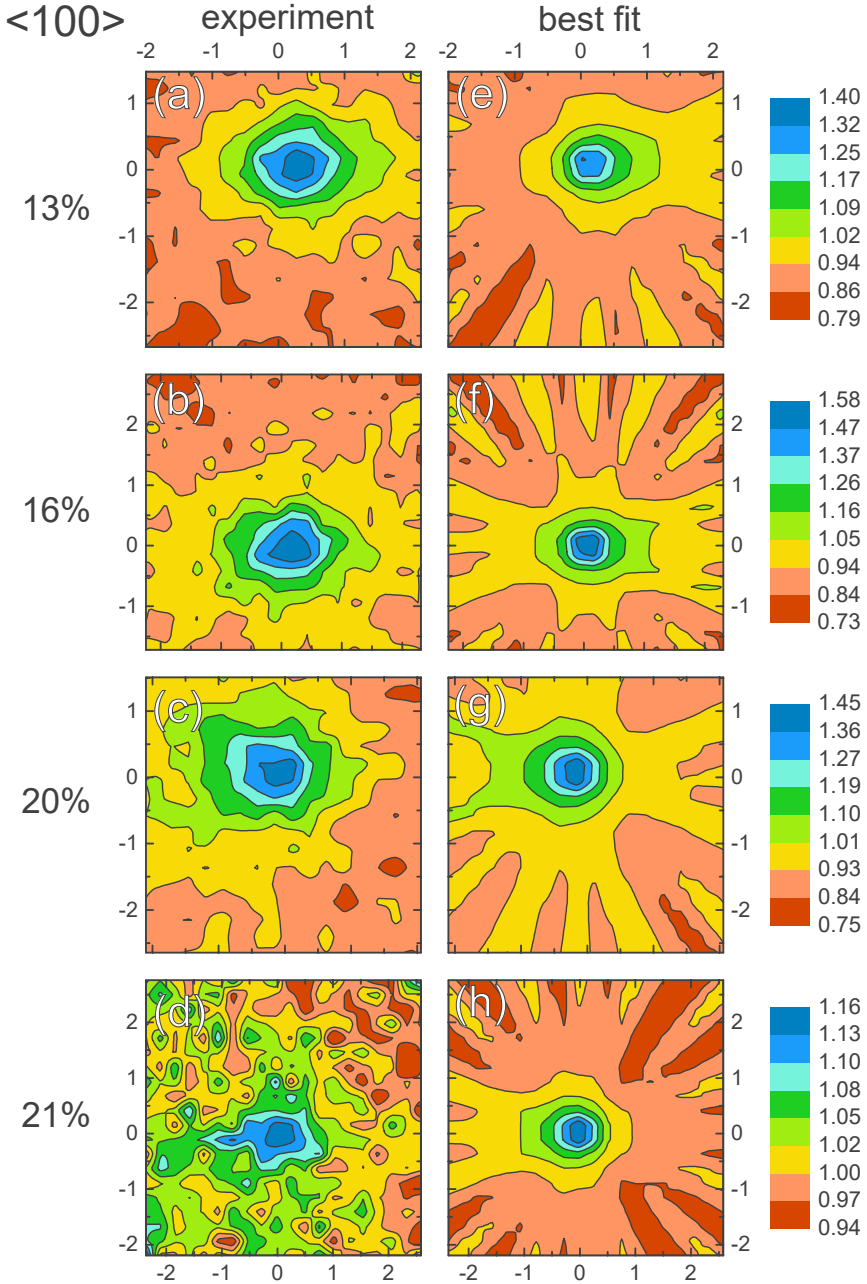


Figure 8.13: (a)-(d) Normalized experimental β^- emission channeling patterns in the vicinity of $\langle 100 \rangle$ direction in (Ge,Mn)Te films at 100 K, as a function of Mn content, and corresponding best fits (e)-(h).

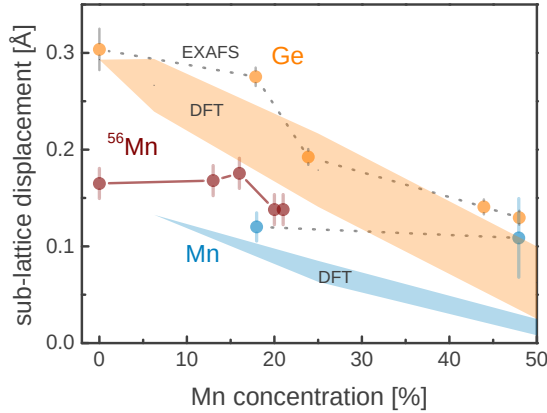


Figure 8.14: Displacement of Ge and Mn sub-lattices as a function of Mn concentration in (Ge,Mn)Te films grown on BaF₂ substrates. The shaded areas represent **DFT** calculations and the dotted lines **EXAFS** results at 5 K, both extracted from Ref. 129. Full lines plot the ⁵⁶Mn emission channeling results on (Ge,Mn)Te samples measured at 100 K, presumably in the **FE** phase, and fitted to *manybeam* simulations with a Ge displacement according to **EXAFS**.

fits in the vicinity of $\langle 100 \rangle$ direction at 100 K for (Ge,Mn)Te films as a function of Mn content. In addition, Table 8.6 compiles the best fitting ⁵⁶Mn sub-lattice displacement and site-fractions for five Mn concentrations in (Ge,Mn)Te. Experimental patterns were fitted to a selection of *manybeam* simulations prepared with different Ge sub-lattice displacements, $\Delta r(\text{Ge})$, according to Ref. 129. Since in Ref. 129 the $\Delta r(\text{Ge})$ values obtained from **DFT** calculations and from **EXAFS** measurements do not fully agree, our analysis considered both cases. Additionally, in each set of simulated patterns the ⁵⁶Mn displacement along the $[111]$ axis was varied, corresponding to lattice sites between S_0 and S_A (cf. sec. 8.2.2.1). The results are summarized in Table 8.6. Within error, the $\Delta r(^{56}\text{Mn})$ values obtained using the input from **DFT** calculations and **EXAFS** data, are the same for a given Mn concentration. This is in line with what was observed for GeTe films (section 8.3.2).

The best fitting values for $\Delta r(^{56}\text{Mn})$ present in Table 8.6 show that the ⁵⁶Mn lattice displacement in epitaxial (Ge,Mn)Te layers is constant at $\Delta(^{56}\text{Mn}) = 0.17 \pm 0.03 \text{ \AA}$, up to a 16% Mn content. For 20% and 21%, a small decrease is

observed, although almost within the error bar. Figure 8.14 plots the best fitting Mn sub-lattice displacement as a function of Mn content in (Ge,Mn)Te layers, and compares them to the Ge and Mn sub-lattice displacements obtained from DFT calculations and EXAFS measurements (adapted from Ref. 129). The decrease in the both Ge and Mn sub-lattice displacements, with increasing Mn concentration, for both DFT predictions and EXAFS data, has been interpreted in Ref. 129 as a consequence of the expanding lattice constant with increasing Mn content, which increases the angle α , thus decreasing overall rhombohedral distortion towards a cubic lattice. Moreover, the difference in displacement for Ge and Mn sub-lattices is attributed to the different electronic structures of both cations. The half-filled 3d shell of Mn contributes to the chemical bonding, strengthening the bonds in the $\langle 100 \rangle$ direction and positioning the Mn atoms towards a more central site, surrounded by Te atoms.²³⁵ This effect is absent for Ge atoms, as the two 4s electrons of Ge^{2+} ions give rise to short-range repulsive forces, resulting in a larger local lattice distortion. Comparing the emission channeling results for the fit of $\langle 100 \rangle$ experimental patterns to *manybeam* simulations with the results from Ref. 129, we observe that the best fit values for $\Delta r(^{56}\text{Mn})$ are in disagreement with DFT calculations, and in (partial) agreement with EXAFS data at the two highest Mn concentrations. In line with the arguments of Kriegner *et al.*,¹²⁹ this enhancement in Mn displacement shifts is likely due to the epitaxial strain imposed by the substrate, which are not accounted for in DFT calculations. This disagreement could also be due to an overestimation (in the DFT calculations) of the contribution of the Mn 3d electrons to the chemical bonding; however that does not directly explain why the disagreement increases with increasing Mn concentration. As the Mn content increases, the intrinsic FE displacements become smaller, and thus the effect of the epitaxial strain may become more significant. Additionally, a large concentration of Ge-vacancies, which provide the magnetism-mediating holes, may also play a role in the lattice distortions.¹⁴⁸ This has not yet been investigated.

The minor difference between our best fit values for $\Delta r(^{56}\text{Mn})$ and the EXAFS values from Ref. 129 may result from the thermal expansion of the (Ge,Mn)Te lattice. EXAFS measurements were performed at 5 K, while emission channeling

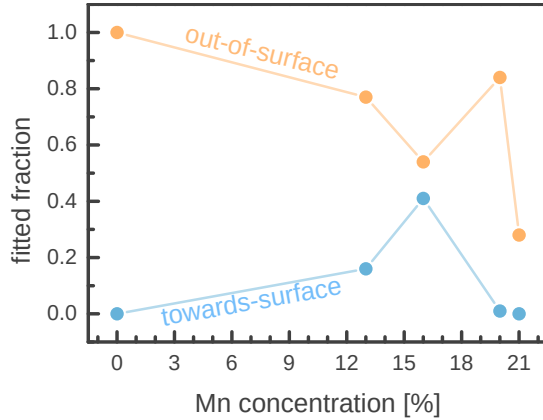


Figure 8.15: Best fit ^{56}Mn fitted-fractions corresponding displacements in opposing orientations. Fractions depict a predominance of crystalline domains with a out-of-surface $[111]$ sub-lattice displacement.

experiments were performed at 100 K. Supplementary XRD data from Ref. 129 show a linear increase of lattice parameter in (Ge,Mn)Te films with increasing temperature, which might slightly change Mn sub-lattice displacement between 5 K and 100 K.

Analogously to the lattice location of ^{56}Mn in GeTe films, the Mn sub-lattice displacement direction in (Ge,Mn)Te films can be inferred from the fitted fractions of ^{56}Mn probes along opposing orientations. Fig. 8.15 plots the fitted fractions of ^{56}Mn probes for displacements towards and out-of-surface, and shows that a majority of radioactive probes occupy lattice sites displaced along the out-of-surface $\langle 111 \rangle$ direction, in good agreement with the XRD trends discussed in Ref. 129. This points towards the predominance of a spontaneous ferroelectric polarization in the studied concentration range, which is coupled with the preferential orientation of the domains in (Ge,Mn)Te films with a sub-lattice displacement direction along the $\langle 111 \rangle$ out-of-surface direction. As mentioned above for GeTe, although it is not possible to identify the origin based on our data, this spontaneous FE polarization at 100 K is likely related to the broken inversion symmetry at the film surface or interface.

Although the results plotted in Fig. 8.15 follow a common trend, two data

points require additional attention, namely for (Ge,Mn)Te doped with 16% (sample f) and 21% Mn (sample h). In sample (f), best fit displacements for both orientations yield ^{56}Mn fitted fractions close to 0.5. This indicates there is an almost equal amount of domains oriented towards and out-of-surface. Figures 8.13(b) and 8.13(f) further illustrate this effect as features of both orientations are present in the experimental pattern (b) and reproduced in the best fit (f), contrary to patterns for other samples. We believe that this deviation is due to a lower crystalline quality of sample (f), namely sample aging (e.g. oxidation or Te loss between the growth and EC measurement).

Sample (h), (Ge,Mn)Te doped with 21% Mn, belongs to the same batch as sample (f), and may therefore exhibit the same issues as mentioned in the previous paragraph. However, Fig. 8.15 shows another effect: the fitted fraction is significantly lower than for 13% and 20% (Ge,Mn)Te samples. In Fig. 8.13(d) and Fig. 8.13(h) this decrease in fitted ^{56}Mn fraction is illustrated by the significantly lower channeling effects compared to other concentrations. While this can partially be explained by the possible sample aging, the weakening of the rhombohedral distortion with increasing Mn concentration is likely to also play a role. As described in section 1.3.2, the rhombohedral distortion in (Ge,Mn)Te persists up to $x_{\text{Mn}} = 0.3$, above which the crystal lattice becomes cubic. Additionally, an increasing Mn concentration changes the strain and thermal expansion properties, which is expected to reduce Ge and Mn sublattice displacements.¹²⁹ These two effects combined allow for distortions along (nearly) equivalent $\langle 111 \rangle$ directions. Hence, a (Ge,Mn)Te film grown at these concentrations is likely to display domains oriented along various $[111]$ axes, i.e. not only the surface $[111]$ direction. This effect is reported in Ref. 129, where different $[111]$ -titled domains become more populated in (Ge,Mn)Te films grown with Mn concentrations above $\sim 20\%$. However, only distortions along the surface $[111]$ were considered in our simulations. This limitation may thus explain why the fitted fraction(s) are significantly lower than for the other samples, for which the constraint (distortions only along the surface $[111]$) is more valid.

8.4.1 Summary

The experiments presented in this chapter demonstrate that the emission channeling technique can have sufficient precision to determine sub-ångström displacements of atoms in a rhombohedral distorted lattice. By carefully optimizing the experimental parameters, the *manybeam* simulations and the fitting procedure, we observed that Mn in (Ge,Mn)Te films occupies Ge-substitutional sites with a smaller shift along the out-of-surface $\langle 111 \rangle$ direction than the Ge sub-lattice. We further observed that this displacement decreases with increasing Mn content, on par with the decreasing rhombohedral distortion. As the material structure approaches a cubic configuration with increasing Mn concentration, the difference between out-of-surface $\langle 111 \rangle$ and other tilted $\langle 111 \rangle$ directions decreases, leading to the equal population of crystalline domains with different sub-lattice displacement directions. This effect challenges the current implementation of the emission channeling technique for determining the sub-lattice displacement of Mn atoms in (Ge,Mn)Te at higher concentrations, limiting further investigations within the multiferroic phase. The possibility of applying magnetic fields at lower temperatures would allow us to magnetize and (depending on the Mn concentration and temperature) polarize the films, allowing for a more precise estimation of the sub-lattice displacement in a wider range of parameters within the phase diagram of (Ge,Mn)Te. Nevertheless, these measurements provide unambiguous evidence of the strong interplay between the local rhombohedral distortion and the sub-lattice displacement experienced by both Ge and Mn atoms in (Ge,Mn)Te.

Chapter 9

Discussion

This chapter brings together the research described in this thesis, drawing a more general picture of the field and addressing the objectives outlined in section 2. It is not intended to repeat all the elements discussed in the previous chapters, but to go beyond, discussing some aspects from a broader perspective, and others which only emerge as the thesis results are considered as a whole.

Section 9.1 deals with the local structure of Mn dopants in dilute magnetic semiconductors, exploring the mechanisms behind the thermal stability of Mn dopants in (Ga,Mn)As and related compounds. This section discusses further the interplay between Mn interstitial out-diffusion and Mn segregation towards achieving high Curie temperature in dilute and hybrid systems; a comment is also made regarding the unexpected incorporation of Mn in anion-substitutional sites.

Section 9.2 focuses on the Mn local structure in multiferroic (Ge,Mn)Te, discussing the relation between the displacement of Ge and Mn sub-lattices and the macroscopic ferroelectric and ferromagnetic properties.

Finally, section 9.3 comments on the limitations of the emission channeling technique in the research described in this thesis and explores a few areas for

future work.

9.1 Local structure of Mn-doped dilute magnetic semiconductors

In sections 4 to 7 the role of the Mn lattice location and its thermal stability was investigated as a function of Mn concentration, from the pure semiconductors GaP, GaAs and GaSb, to the several percent concentration in (Ga,Mn)As, quaternary (Ga,Mn)(As,P) and (Ga,Mn)(As,Sb), and (Ga,Mn)Sb. Both regimes have characteristic diffusion mechanisms at play, which are deeply connected with the thermal stability of Mn dopants in two different lattice sites: the cation-substitutional site, S_{Ga} or S_{A} , and the tetrahedral interstitial site coordinated by four anion nearest neighbors, T_{B} .

The incorporation of interstitial Mn, or Mn_i , is greatly reflected in the structural and magnetic properties of Mn-doped III-V semiconductors, as Mn atoms in these sites act as double donors, effectively compensating both the magnetic moment and charge carriers provided by substitutional acceptors. Accordingly, understanding the nature of the interstitial sites as well as their formation mechanisms plays a significant role in the development of a high Curie temperature dilute phase. However, it is the interplay between the thermal stability of both interstitial and substitutional Mn dopants which ultimately determines the structural and magnetic properties of the semiconductor.

9.1.1 The interstitial site

The first step in understanding the mechanisms behind interstitial diffusion in (Ga,Mn)As and related compounds, is to establish the nature of the interstitial impurity, i.e. its lattice site, local structure and thermal stability. The lattice site of interstitial Mn atoms was unambiguously identified as the interstitial tetrahedral site with anion nearest neighbors, or T_{B} , across all III-Mn-V compounds. Furthermore, this site was identified not only in pure GaP, GaAs

and GaSb semiconductors, where Mn_i is isolated, but also in ferromagnetic films of (Ga,Mn)As and (Ga,Mn)Sb, where Mn_i is more likely to be bound in complexes with substitutional Mn (cf. chapters 4 and 7).

The stability of interstitial sites is intimately connected with its local structure, as it depends on the energy barriers surrounding the impurity site. The height of these barriers can be linked with the bond strength between the host atoms, Ga and P, As, or Sb, which defines the lattice constant of the semiconductor as well as the atomic packing. For example, a low barrier will allow the Mn_i atom to easily cross it and stabilize in a position surrounded by higher energy barriers. Consequently, these barriers can result in a different stability of Mn impurities in similar interstitial sites, such as the tetrahedral interstitial site with either cation (T_{Ga}) or anion (T_B) nearest neighbors in a *zincblende* crystal lattice.

This effect has been observed across all systems investigated in this thesis, where Mn impurities in the T_B site were found to be considerably more stable at and above room temperature than the T_{Ga} site. Manganese interstitials in T_{Ga} sites were also investigated in the emission channeling experiments described in chapters 4 and 7, but no fractions were found within error ($< 0.8\%$ of all implanted radioactive probes). While this does not exclude the possibility that Mn dopants can stabilize in T_{Ga} sites during *LT-MBE* growth, with a favorable formation energy, it suggests that the diffusion barrier for migration between T_{Ga} and T_B sites is low and overcome at room temperature. This hypothesis could be further assessed by low-temperature emission channeling experiments, in an attempt to stabilize ^{56}Mn probes in T_{Ga} sites at sufficiently low temperatures.

We can further extend these considerations for interstitial stabilization to the compounds studied in chapter 8, GeTe and (Ge,Mn)Te. First, only Ge-vacancies have been observed in GeTe crystals as intrinsically occurring defects, and no interstitial-like compensating defects similar to Mn_i in III-Mn-V's were found up to Mn solubility limit in (Ge,Mn)Te. Second, the interstitial sites in the GeTe structure ($R\bar{3}m$ space group), are less prone for Mn occupation, compared to the T sites in the GaAs structure, in terms of symmetry and available volume. Third, a distinguished feature of IV-VI compounds are their

large static dielectric constants which are relevant for the screening of Mn potentials.²³⁶ Additionally, unlike III-V semiconductors, IV-VI compounds have less stringent growth conditions due to a lower reactivity between group IV and group VI elements,^{236,237} which makes these materials quite insensitive to the introduction of defects during growth.

Accordingly, the combination of these effects with a large abundance of Ge-vacancies, typical of GeTe films, discards the possible stabilization mechanism similar to Mn_i in III-Mn-V FMS.

9.1.2 Interstitial diffusion

The stability difference between T_{Ga} sites and T_B sites defines a diffusion path for interstitial Mn when sufficient thermal energy is provided to the system ($T_{Ga} \rightarrow T_B \rightarrow T_{Ga} \rightarrow \dots$). The diffusion mechanism in (Ga,Mn)As and related compounds can then be described as an interstitial diffusion process, in which Mn_i jumps through interstitial sites until it becomes immobilized by a Ga-vacancy, interface or secondary-phase (cf. section 5.4.2.2).

In the pure GaP, GaAs, and GaSb semiconductors, this diffusion mechanism depends mostly on the thermal stability of the Mn interstitial site, i.e. when bond strength between cation and anion atoms in the host semiconductor increases, so do the energy barriers for interstitial diffusion, and, consequently, the Mn_i thermal stability. This was observed in section 7.4.2, where the activation energy for interstitial diffusion significantly increases from 1.0 – 1.4 eV in GaSb, to 1.7 – 2.3 eV in GaAs, to 2.0 – 2.8 eV in GaP.

Considering this interstitial diffusion model, it naturally follows that the diffusion of substitutional Mn also depends on the thermal stability of interstitial sites. Provided sufficient thermal energy for Mn atoms to jump from a substitutional to interstitial positions, these will diffuse interstitially through the path outlined above until immobilized. While the diffusion model for the Mn-doped case is more complex than in the pure semiconductors case (and is addressed below), the diffusion mechanism through interstitial sites is the same and was observed in the emission channeling results in (Ga,Mn)Sb presented in section 7.4.4.

In Fig. 7.4(d), after an annealing step of 170°C, the fitted fractions of both substitutional and interstitial ^{56}Mn probes reach a local maximum and minimum, respectively. These inflexion points are prompted by the recovery of the crystal from implantation damage, as Ga-vacancies combine with (i) Ga- and Mn-substitutionals as well as with (ii) diffusing Mn interstitials.^a The recombination with the former group results in an increase in Mn_s fractions, while with the latter in decreasing Mn_i fractions. The subsequent annealing steps illustrate both an increase in interstitial fractions and a decrease in substitutional ones. Because substitutional Mn becomes mobile at these temperatures ($\sim 200^\circ\text{C}$), it jumps to interstitial sites to diffuse interstitially. Due to the short annealing time (10 min), a significant fraction of diffusing Mn becomes trapped and stabilizes in interstitial sites, consequently increasing the fitted Mn_i fractions.

9.1.3 Enhanced manganese diffusion

In chapters 5 and 7 the interstitial diffusion mechanism was found to also depend on the Mn content for Mn-doped III-V semiconductors. Because substitutional and interstitial Mn atoms are incorporated in opposite charged states in (Ga,Mn)As layers and related compounds, they exhibit a Coulomb interaction between one another. Consequently, as the Mn concentration is increased in III-Mn-V, the likelihood that interstitial impurities are coupled with substitutional complexes also increases. This directly increases the thermal stability of interstitial Mn at higher concentrations, as they get trapped in ever more complex configurations (with one, two or more substitutionals). This effect directly hinders their out-diffusion by low-temperature annealing, and constitutes the local structure origin for the antiferromagnetic compensation mechanism observed in ferromagnetic (Ga,Mn)As layers.

However, as the Mn concentration increases, the collective interaction with substitutional Mn atoms which are located further away (compared to those forming the nearest neighbor complexes) also becomes relevant to the diffusion mechanism. Assuming an isotropic and random distribution of substitutional dopants, at higher Mn contents the average distance between substitutional and

^aInterstitial Mn becomes mobile at lower temperatures in (Ga,Mn)Sb than in (Ga,Mn)As.

interstitial atoms is smaller, and for each interstitial Mn atom in a complex with Mn_s , there are increasingly more Mn substitutional neighbors within a few unit cell distances. Accordingly, the Coulomb interaction between the interstitial Mn atoms and the neighboring Mn_s atoms can be sufficiently strong to reduce their thermal stability, i.e. the energy barrier that Mn_i needs to overcome in order to diffuse. Thus, the collective interaction with all neighboring substitutional Mn atoms counteracts that of the binding in complexes with individual substitutional Mn_s , and can ultimately result in an effective decrease in activation energy for interstitial diffusion.

In summary, the interstitial diffusion mechanism in the several percent Mn-doped regime results from two distinct contributions: (i) the interstitial mobility through T_{Ga} and T_{B} sites, and (ii) the competition among the binding of Mn_i atoms in complexes with individual substitutional Mn atoms versus the collective Coulomb interaction with all neighboring Mn_s . This intricate interplay between different contributions to the interstitial diffusion of Mn impurities is also reflected in the activation energy for substitutional Mn diffusion, which changes by a similar amount as for the interstitial diffusion. Ultimately, this effect results in a net decrease in activation energy for diffusion of both substitutional and interstitial Mn atoms, in the Mn-doped III-V semiconductors investigated in chapters 5 and 7, compared to the pure III-V semiconductors.

9.1.4 Structural and magnetic properties

The complex diffusion mechanisms explored here have a direct impact on the thermal treatment of III-Mn-V DMS, resulting in two critical limitations: on the one hand, the binding of interstitial Mn with substitutional Mn complexes limits the minimum annealing temperature at which the out-diffusion and passivation of compensating interstitial impurities is promoted; on the other hand, the enhanced diffusion derived from the interaction between large substitutional Mn fractions induces an onset of Mn segregation at low annealing temperatures. In other words, the different contributions to the diffusion mechanism limit the temperature window at which interstitial Mn impurities can be effectively removed to a particularly narrow range in (Ga,Mn)As layers, consistent with

the partial interstitial reduction observed even in thin films which achieved the highest Curie temperatures.^{22, 25}

On the upper end of the annealing temperature window for Curie temperature optimization is the thermal stability of substitutional Mn atoms, which decreases at higher Mn concentrations. A lower stability of substitutional atoms at low annealing temperatures ($\sim 300^\circ\text{C}$) can be directly linked with Mn segregation into secondary phases. These temperatures are lower than the typical annealing temperatures for secondary-phase formation in ferromagnetic (Ga,Mn)As films reported in literature, $> 500^\circ\text{C}$ (cf. sections 5.4.2 and 7.4.4). However, these low temperatures are still too low to allow for the the formation of well-crystallized MnAs precipitates, resulting instead in disordered non-magnetic Mn-rich nanoclusters embedded in a GaAs:Mn matrix (cf. chapter 6).

Since Mn diffusion is driven through interstitial sites, it largely depends on the atomic packing^b across the III-Mn-V DMS family. This effect was observed in chapter 7 in two different situations: comparing the Mn thermal stability between (Ga,Mn)As and quaternary (Ga,Mn)(As,X) films, X=P or X=Sb, and between (Ga,Mn)As and (Ga,Mn)Sb. Changing the composition of (Ga,Mn)As films through the addition of several % of group V elements, such as P and Sb, with the same 6% Mn concentration, in a decrease in Mn thermal stability as the anion doping changes from P to As to Sb. Here, the higher Mn thermal stability observed in (Ga,Mn)(As,P) layers agrees with the lower Curie temperatures achieved through annealing treatments.^{72, 77} On the other hand, P-doped layers also display a tunable strain which allows for a precise control and switching of magnetic anisotropy.^{69, 73, 103} Since the density of interstitial Mn has been observed to directly influence the strain and the lattice parameter of (Ga,Mn)As layers,²⁰⁰ the tunable strain in (Ga,Mn)(As,P) can also be achieved because of the larger interstitial Mn thermal stability in the system. For (Ga,Mn)(As,Sb) layers a similar effect may occur, in which the presence of Sb atoms may rearrange the Mn_i redistribution, resulting in a larger anisotropic magnetoresistance along the $[1\bar{1}0]$ and $[110]$ crystalline directions.⁷⁰ Unfortunately, the introduction of Sb atoms induces disorder and more defects during growth of (Ga,Mn)(As,Sb)

^bThe atomic packing is larger in a semiconductor compound with a smaller lattice constant, a consequence of stronger cation-anion bond strength.

layers, ultimately reducing maximum achievable Curie temperature.⁷¹

In the case of (Ga,Mn)Sb layers, the observed Mn thermal stability is significantly lower than its counterpart (Ga,Mn)As (cf. section 7.4.4). There is a considerable decrease in activation energy for interstitial Mn diffusion which is consistent with a lower stability of T_{Sb} sites compared to T_{As} sites in (Ga,Mn)As. Consequently, also the activation energy for substitutional diffusion significantly decreases. This lower stability can already be significant during LT-MBE growth of (Ga,Mn)Sb crystals, as both the absence of interstitial compensation and the presence of MnSb secondary phases have been reported in as-grown layers.^{80,82,86,87}

In summary, two fundamental aspects are required for the incorporation of interstitial Mn dopants in III-Mn-V FMS: (i) the availability of low-formation energy interstitial sites,⁴⁸ and (ii) the thermal stability of interstitial impurities during growth in said sites. The first is a direct consequence of the crystalline structure itself, as tetrahedral sites in *zincblende* $F\bar{4}3m$ have the same symmetry as substitutional sites, reducing defect formation energy at these sites. The second, the thermal stability of interstitial sites at growth temperatures is also dependent on the Mn concentration and on the interaction between oppositely charged defects. (Ga,Mn)Sb has a larger lattice constant and electrical permittivity than (Ga,Mn)As, weakening the Coulomb interaction between Mn_{S}^- and $\text{Mn}_{\text{I}}^{2+}$, thus decreasing interstitial thermal stability in the lattice at growth temperature, and, ultimately, regulating the stabilization of Mn dopants in interstitial sites.

9.1.5 Prospects for room-temperature ferromagnetism

Tuning T_{C} in III-Mn-V FMS by engineering both anion composition and Mn concentration is largely an exercise of carefully balancing the thermal stability of Mn with charge carrier density and segregation into secondary phases. Achieving high Curie temperatures requires not only a very precise control and understanding of the different phenomena that influence its magnetic and electric properties, but also a critical balancing between Mn formation (interstitial), diffusion, and segregation (substitutional). To this end, we observed that among

the III-Mn-V systems, (Ga,Mn)As provides the best balance between the local structure, electronic and magnetic properties.

Achieving above room-temperature ferromagnetism in these compounds remains a formidable challenge, so far being largely dependent on the traditional thermal annealing methodology. Furthermore, there might be a fundamental limit to the maximum T_C achieved for fully substitutional Mn incorporation in (Ga,Mn)As layers,⁵² ultimately restricting the functionality of (Ga,Mn)As to below room-temperature spintronic applications.

9.1.5.1 Interstitial-to-substitutional conversion

Assembling the complex understanding of local structure and magnetism in III-Mn-V FMS described in this thesis with the work presented in Refs. [90, 94] may provide an alternative strategy for Curie temperature maximization in these compounds. Refs. [90, 94] investigated the lattice location of ^{56}Mn in GaAs, observing a decrease of interstitial fractions coincidental with an increase in substitutional ones at an annealing temperature of 400°C. In these experiments, as interstitial Mn becomes mobile, there is a large probability of combination with Ga vacancies produced during implantation, effectively converting into a substitutional fraction. This effect is not observed at higher Mn concentrations, in the experiments described in this thesis, where the Ga-vacancies produced during implantation of ^{56}Mn quickly recombine with the large amount of stable ^{55}Mn in (Ga,Mn)As and (Ga,Mn)Sb at low annealing temperatures. This greatly decreases the number of Ga-vacancies available for interstitial ^{56}Mn , limiting our ability to observe the recombination process in the EC data.

Harnessing this effect in Mn-doped III-V FMS could provide a path to increasing the effective substitutional fraction, i.e. uncompensated magnetically active Mn_s . This would require producing Ga-vacancies which can be filled by interstitial Mn. A possible implementation of this mechanism would be to irradiate (Ga,Mn)As using light ion beams to produce Ga-vacancies during thermal annealing at temperatures where Mn_i is mobile ($\sim 200^\circ\text{C}$). In a study by Zhou *et al.*,⁴⁰ the effect of He-irradiation in (Ga,Mn)As and (Ga,Mn)(As,P) layers was investigated as a function of *displacement per atom* (DPA), which is a better representation

of the effect of irradiation on material properties than ion fluence (dosage). This irradiation mostly affected the charge-carrier concentration, decreasing as a function of DPA. It was shown that ferromagnetic T_C decreases with increasing DPA, mainly due to a decrease in hole concentration and compounding disorder in the (Ga,Mn)As layers. However, these irradiation experiments were performed at room temperature. Fine tuning these experiments by performing He-implantation at selected temperatures such that a significant lattice recovery from the implantation damage would be induced, as well as a conversion of interstitial Mn fraction to substitutional through recombination with newly generated Ga-vacancies, could provide a pathway towards full substitutional Mn incorporation in (Ga,Mn)As.

However, there are a few plausible downfalls to this method, namely connected with the introduction of damage and defects in the (Ga,Mn)As lattice. Since As and Ga are close in atomic mass, ion-irradiation will knock out both cation and anion atoms alike, likely promote the formation of both stable defects observed in GaAs semiconductors, Ga-vacancies and As-antisites.^{223,238} Additionally, for each Ga-vacancy there is a Ga-interstitial formed during implantation, which will directly compete with diffusing interstitial Mn impurities in the recombination with vacancies. Both processes could hinder the conversion of Mn from interstitial to Ga-substitutional sites, limiting the extent to which T_C can be optimized through this method.

9.1.6 Anion-substitutional Mn in III-V semiconductors

In compound semiconductors, the lattice site occupied by an dopant is generally determined by matching its chemical similarity, ionic size and electronegativity, with the host atoms. *3d*-transition metal dopants in the III-V family have similar properties to the host cation, which naturally leads to its incorporation in cation-substitutional sites, such as Mn_{Ga} in GaN,^{194,195} GaAs,^{90,94} GaP and GaSb (cf. chapter 7). In addition, Mn dopants were found to also occupy interstitial sites, particularly, tetrahedral sites coordinated by the anion as nearest neighbors in the III-V semiconductors investigated in this thesis, GaP, GaAs and GaSb.

Surprisingly, the emission channeling experiments described in chapter 7 across the III-V semiconductor family also identified a third unexpected lattice site that Mn dopants can occupy in GaP – the anion-substitutional site. The incorporation of Mn in anion-substitutional sites is still poorly understood, with little to no theoretical studies considering its existence in these compounds. There are, however, a few experimental observations of Mn anion-substitutionals in another semiconductor of the III-V family, GaN. The work reported in Ref. 221 reports on N-substitution by Mn dopants in *zinc-blende* GaN grown by *LT-MBE* in N-poor conditions. Through the XAFS technique they have identified fractions of up to 75% of Mn dopants in N-substitutional sites, an sufficiently high fraction to allow detection. In addition to these studies, emission channeling investigations described in Refs. [194–196] also reported Mn incorporation in N-substitutional sites in GaN up to very high annealing temperatures, 900°C, portraying their high thermal stability comparable to Ga-substitutional sites. The occupation of anion-substitutional sites has been addressed in several other cases: in GaN, minority anion sites were observed for Mn¹⁹⁵ and Co,¹⁹⁶ but not for Fe^{196,222} and Ni^c; in ZnO, which is a II-VI semiconductor with properties very similar to GaN, minority anion sites were observed for Mn,¹⁹⁴ Co^{194,196} and Ni,¹⁹⁷ but not for Fe²³⁹ (the majority of Mn, Fe, Co and Ni in GaN and ZnO occupies cation sites, Ga and Zn). Accordingly, the incorporation of transition metal dopants cannot be directly linked to the non-equilibrium process of ion implantation, as it was not consistently observed for other *3d*-transition metal isotopes.¹⁹⁶

Comparing the results from these studies suggests that the stabilization of Mn dopants in anion-substitutional sites is directly linked with its local structure, i.e. neighboring atoms and/or vacancies. Thus, incorporation in these sites may be favored in the combination of different effects: at different charge states, such as cation-antisites, or in the presence of neighboring Ga-vacancies, or in the case of an abundance of group V vacancies. Like cation antisites in III-V semiconductors, it is possible that Mn anion-substitutionals become stable with varying charge states in GaN and GaP, and unstable for narrower-gap GaAs and GaSb, depending mostly on growth conditions (metal-rich or metal-poor)

^cUnpublished data

as well as on the position of the Fermi level.^{223–225, 240–242} Another factor that may play a role in the formation energy of anion-substitutional is the presence of either cation or anion vacancies, natural defects resulting from the non-equilibrium process of ion implantation. According to Ref.²³⁸ the formation energy of vacancies in III-V semiconductors favors the formation of cation vacancies under stoichiometric conditions, which might contribute to the stabilization of Mn in anion-substitutional sites in the presence of one or two neighboring Ga-vacancies.^d On the other hand, a significant fraction of anion vacancies is also required and can effectively increase the likelihood of Mn occupying anion sites. First principles calculations in Refs. [238, 241, 243] show a general trend across the III-V semiconductor family, in which the difference between formation energies of cation and anion vacancies increases from GaN to GaSb, which might be correlated with the formation of higher concentrations of anion vacancies in the lower mass semiconductors.

The possibilities outlined above can be tested via density functional theory calculations of the formation energies for Mn in anion-substitutional sites in GaN, GaP, GaAs and GaSb at various charge states and in the presence of a sufficient amount of cation and anion vacancies.

^dThis is assuming that: (i) ion implantation pins the Fermi level to the middle of the band-gap in III-V semiconductors, and (ii) that the semiconductors are intrinsic and undoped.

9.2 Local structure of multiferroic Rashba semiconductor (Ge,Mn)Te

Germanium telluride is a conventional semiconductor with a wide range of applications in the thermoelectric, ferroelectric and phase-change material fields.¹³⁰ Particular to this material is the peculiar *resonant* bonding between Ge and Te atoms, which forces the crystal lattice to stabilize in a distorted configuration under fully stoichiometric conditions and at room temperature, with alternated short strong bonds and long weaker ones.^{135,136} This distortion induces both a highly delocalized and spin-polarizable p electron density and a stabilization of the crystal in a rhombohedral distorted $R\bar{3}m$ crystal structure. This rhombohedral distortion grants GeTe its ferroelectric properties, with the ferroelectric polarization direction along the alternating long and short bonds. In other words, ferroelectricity stems from the shift between Ge and Te sub-lattices, which no longer share the same center of charge. From the reference frame of the Te sub-lattice this shift can be considered as a displacement of the Ge sub-lattice along the $[111]$ axis, breaking crystalline inversion symmetry. Moreover, it is the interaction between the electric field induced by the inversion symmetry breaking and spin-polarized charge carriers travelling parallel to the surface which induces a giant Rashba splitting in the spin-bands (cf. section 1.3.1).¹⁵⁵ Consequently, one can conclude that the Rashba splitting is strongly dependent on the sub-lattice displacement magnitude and direction.

In multiferroic Rashba semiconductor (Ge,Mn)Te additional complexity is introduced to GeTe semiconducting and ferroelectric properties through the incorporation of Mn dopants. Assuming a random and dilute stabilization of Mn dopants in Ge-substitutional sites, a long range $p - d$ ferromagnetic interaction emerges, resulting in a ferromagnetic phase with increasing Curie temperature up to Mn solubility, $x_{\text{Mn}} \sim 0.50$. Moreover, the interaction between the $p - d$ magnetization and the spin-polarized charge carriers in (Ge,Mn)Te layers opens a tunable Zeeman gap of about 100 meV at higher Mn contents.³² Because Mn atoms have a half-filled $3d$ electronic shell, their chemical bonding with neighboring Te atoms leads to a more central lattice site than Ge cations,

i.e. the displacement of the Mn sub-lattice should be smaller than that of the Ge sub-lattice. This displacement was directly observed in the emission channeling analysis described in chapter 8, which measured a smaller Mn sub-lattice displacement in both GeTe and (Ge,Mn)Te films with Mn contents up to $x_{\text{Mn}} \sim 0.21$, in the ferroelectric phase, at 100 K.

As the Mn concentration is increased in (Ge,Mn)Te, the prevalence of stronger Mn-Te bonds is also higher and effectively reduces the rhombohedral distortion of the Ge and Te sub-lattices, characterized by an angle between unit cell vectors of $\alpha < 90^\circ$. Accordingly, the rhombohedral distortion of the Ge and Te sub-lattices decreases up to Mn contents $x_{\text{Mn}} \sim 0.30$, above which it is no longer measurable and can be assumed to vanish ($\alpha = 90^\circ$). However, this decrease in rhombohedral distortion may not be directly linked to a decrease in the displacement between cation and anion sub-lattices, i.e. above the $x_{\text{Mn}} \sim 0.30$ threshold, the lattice remains “distorted” due to the displacement between Ge (Mn) and Te sub-lattices.^{129,169} This displacement has a significant role in the ferroelectricity of (Ge,Mn)Te crystals, and is expected to persist up to $x_{\text{Mn}} \sim 0.30$, concentration above which the ferroelectric polarization vanishes.¹²⁹

The emission channeling experiments described in section 8.4 were not sufficiently sensitive to the Ge sub-lattice displacement and, therefore, could not quantify its (possible) change as a function of Mn concentration. On the other hand, the displacement of the Mn sub-lattice was determined with high precision, yielded a nearly constant value across the probed concentrations, up to $x_{\text{Mn}} \sim 0.21$, which is in good agreement with the strong Mn-Te bond in the structure of (Ge,Mn)Te, albeit seemingly independent from the decreasing rhombohedral distortion in the ferroelectric phase.

At a more macroscopic level, the decreasing rhombohedral distortion in (Ge,Mn)Te appears to have significant impact on both its magnetocrystalline anisotropy and its ferroelectric polarization direction, i.e. above $x_{\text{Mn}} \sim 0.20$ the easy magnetization axis rotates from the [111] surface normal towards other oblique [111] axes.¹²⁹ As the Ge, Mn and Te sub-lattice become cubic^e,

^ealthough the crystal remains rhombohedral and distorted due to the sub-lattice displacement

oblique [111] axes are equivalent to the [111] surface normal, which influences the distribution of crystalline domains oriented along each direction. While below $x_{\text{Mn}} \sim 0.20$ there is a preferential alignment of crystallites along the [111] surface normal, above there is gradual equalization on the population of differently aligned crystalline domains up to $x_{\text{Mn}} \sim 0.30$.^{34,129} This effect was visible in the Mn sub-lattice displacement investigated in chapter 8 in both GeTe and (Ge,Mn)Te films. At 100 K, the displacement of the Mn sub-lattice was found to be predominantly oriented along the $\langle 111 \rangle$ out-of-surface direction for Mn concentrations up to $x_{\text{Mn}} \sim 0.20$. This pinning along one orientation of the [111] axis can be most likely attributed to an interaction of the GeTe or (Ge,Mn)Te layer with the BaF₂ substrate during growth. Additionally, while the uncertainty in the Mn concentration and in the precision of the emission channeling experiments does not allow to discriminate between 20% and 21% Mn-doped samples, there is a significant change in the analysis of the latter concentration. This was attributed to the population of differently oriented crystallites, which could not be accounted for in the analysis. This effect at Mn concentrations above $x_{\text{Mn}} \sim 0.20$ is further supported by the work described in Ref. 34, where magnetic-field induced switching of ferroelectric domains has been observed in ferromagnetic resonance experiments. They observe a small fraction of ferroelectric domains which remain oppositely polarized after magnetic-field switching, and that can be attributed to the population of tilted [111] domains, which “freeze” some of the FM moments, particularly evident for higher Mn concentrations in (Ge,Mn)Te.

The experiments performed in this thesis only addressed the Mn sub-lattice displacement in the ferroelectric phase of (Ge,Mn)Te films. However, because the Mn sub-lattice displacement has been observed to remain constant from 5 K up to room temperature,^f the results presented here can be extended to the multiferroic phase. Accordingly, these results show the local structure contribution of the interplay between ferroelectric polarization and magnetization directions. For Mn concentrations below $x_{\text{Mn}} \sim 0.20$, the rhombohedral distortion and Ge sub-lattice displacement pin the Mn sub-lattice to displacements along the same direction. This effect combined with the preferential orientation of different

^fUnpublished EXAFS data in (Ge,Mn)Te films with Mn concentrations up to $x_{\text{Mn}} \sim 0.20$ observed a constant Mn sub-lattice displacement in this temperature range.

crystallites along the $\langle 111 \rangle$ out-of-surface direction ultimately define the basis for the magnetoelectric coupling in (Ge,Mn)Te layers. This coupling between FE and FM properties has been demonstrated in this concentration range by both a magnetic-field switching of the ferroelectric polarization,³² as well as by an electric-field control of the magnetization,³³ and promises a controllable tuning of both Zeeman and Rashba effects in (Ge,Mn)Te crystals.

9.2.1 Prospects for a room-temperature multiferroic phase

The multiferroic phase is currently limited to below 100 K, i.e. well below room-temperature. Higher Mn concentrations increase the critical temperature for ferromagnetism, but decrease it for ferroelectricity. Accordingly, only increasing the ferromagnetic Curie temperature T_C for Mn contents below 30% could provide a pathway towards higher multiferroic functionalization at operational conditions above room-temperature. Further investigations are required on the mechanisms which can increase the $p-d$ ferromagnetic Curie temperature in (Ge,Mn)Te, namely on the effect of tuning the concentration of Ge-vacancies which provide spin-polarized mediating charge carriers.

Achieving above room-temperature functionalization of multiferroic Rashba semiconductors has also been proposed by doping GeTe films with other transition metals, such as chromium (Cr) and iron (Fe). First principles studies on the incorporation of different transition metals in GeTe projected a higher solubility than in III-V semiconductors, which can lead to higher ferromagnetic Curie temperatures, particularly in Cr-, Fe- and Mn-doped crystals.^{148,165} In these studies, Cr-doped GeTe has been proposed to achieve ferromagnetism above room-temperature for concentrations close to 50%, through a double-exchange ferromagnetic interaction, in contrast with the $p-d$ ferromagnetism of (Ge,Mn)Te. Experimentally, different magnetic states have been observed in (Ge,Cr)Te crystals as a function of Cr content,²⁴⁴ with a high Curie temperature ferromagnetic state reaching $T_C = 180$ K for a fairly low Cr content of $x \approx 0.06$.²⁴⁵ In Fe-doped GeTe with 2% dopant concentrations, a $T_C \sim 140$ K has been observed, together with a reversible control of ferromagnetism, alternating between short-range and long-range ferromagnetic

exchange interactions between amorphous and crystalline phases.²⁴⁶

While these studies portray promising prospects for achieving an above room-temperature ferromagnetism at low dopant concentrations, further research on the electronic, magnetic and structural properties of such systems will be required. In particular, and in accordance with the first principle studies in Ref. 148, Cr- and Fe-doped GeTe are promising systems in which to investigate the interplay between the ferroelectric and ferromagnetic properties, as high Curie temperatures have been observed at low concentrations and are predicted to increase toward higher dopant concentrations.

9.3 Limitations of the emission channeling technique

This thesis has essentially focused on the use of the emission channeling technique for the study of the local structure of Mn atoms in two families of ferromagnetic semiconductors, DMS and MUFERS. This included comparing our results to those of previous studies using different techniques and minimizing possible sources of error. Here we extend that discussion towards the limitations of the emission channeling technique, in particular on the determination of the lattice location of Mn atoms in FMS.

Emission channeling requires the introduction of (often short-lived) radioactive isotopes into single-crystalline samples or thin films, for which the only feasible method is ion implantation. Although typical implanted fluences in an EC experiment are negligible compared to existing Mn contents in pre-doped FMS films (in the several % Mn range), the resulting lattice sites occupied by ^{56}Mn radioactive probes can differ from the stable ^{55}Mn sites. Two factors play a significant role in this possibility and are intimately connected with ion-implantation: (i) its non-equilibrium nature, and (ii) the introduction of lattice defects.

The non-equilibrium nature of ion-implantation is connected with the impinging atom energy, which is several orders of magnitude larger than conventional

doping/growth techniques: for example, for [LT-MBE](#) this energy is of the order of 0.1 eV, for pulsed laser deposition it is 10 eV, and for ion implantation it is 100 keV. Incorporating dopants at energies far from equilibrium allows for the population of lattice sites associated with high formation energies, which would not normally be available at lower energies. An example of such a lattice site could be the Mn-antisite observed for GaN and GaP, described earlier in this chapter (cf. section [9.1.6](#)).

Moreover, particle bombardment at high energies creates lattice defects in the material, or beam-induced damage, with a considerably larger concentration than conventional doping/growth methods. These defects may play a role in the lattice location of dopants and impurities, by changing the Fermi-level of the material, for example, or by forming dopant complexes which also affect their thermal stability. Additionally, beam-induced damage increases with implanted fluence, reducing crystal quality and deteriorating channeling effects, ultimately imposing a limit on the concentration regimes which can be studied through emission channeling.

Finally, electron channeling features from typical emission channeling experiments can provide additional site-specific information, which allows for an unambiguous lattice site determination. However, electrons are also easily scattered in the film, substrate and within the experimental chamber, resulting in significant contributions towards the background. This inevitable electron scattering combined with beam-induced damage in the material strongly influences dopant lattice site determination, particularly when working close to the technique's precision, as in chapter [8](#). Other ion-beam techniques, such as Rutherford backscattering spectrometry (RSBS/c) or particle induced x-ray emission (PIXE-c), performed using a similar approach to emission channeling could present themselves as a strong solution for a more accurate lattice site determination, with the advantage of no beam-induced damage, but with the caveat of limited resolution to low Mn content materials.

Chapter 10

Conclusions

This thesis focused on the local structure of Mn dopants in two families of Mn-doped ferromagnetic semiconductors: III-Mn-V **dilute magnetic semiconductors** and **multiferroic Rashba semiconductor** (Ge,Mn)Te. From a fundamental point of view, the local structure of Mn dopants in semiconductors directly influences the lattice sites they can occupy, as well as their thermal stability in the same sites. While not investigated directly in this thesis (for the most part), the local structure has an indirect role on the electronic, magnetic and even multiferroic properties of the Mn-doped semiconductors.

The first part of this thesis dedicated particular attention to the lattice location and thermal stability of Mn impurities in “conventional” **dilute magnetic semiconductors**, such as (Ga,Mn)As and similar Mn-doped III-V semiconductors, exploring the limiting factors in the quest towards room-temperature operation. The incorporation of Mn dopants in interstitial sites in these compounds is one of the major challenges in achieving higher Curie temperatures, which is only partially resolved through thermal treatment close to growth temperature. The stability of Mn dopants in interstitial sites is largely dependent both on the local structure of the site and on the Mn concentration.

Across the III-Mn-V **DMS** family, the preferred interstitial site is the tetrahedral

interstitial site coordinated by four anion atoms. The stability of Mn atoms in these sites increases with the atomic packing of the semiconductor lattice, i.e. in smaller unit cell structures the energetic barriers keeping the interstitial site stable are larger. This effect is largely visible in (Ga,Mn)As, where the interstitial Mn has a significant impact on the ferromagnetic properties of the layers.²⁰⁰ In contrast, (Ga,Mn)Sb layers do not show any signs of interstitial compensation.⁸⁰ This divergence was observed in this thesis through the thermal stability of interstitial Mn, which is larger in the former material than in the latter.

The thermal stability of Mn dopants severely limits the usefulness of thermal annealing across the III-Mn-V as a means of achieving higher ferromagnetic Curie temperatures from **two** different perspectives. On the one hand, the thermal stability of **interstitial Mn** impurities determines a minimum annealing temperature required to promote their out-diffusion, as the stability of these defects is also largely dependent on the Mn concentration. At larger Mn contents, Mn interstitials can be isolated or antiferromagnetically bound to substitutional Mn dopants. While this binding directly leads to an increase in energy required for thermal diffusion, the Coulomb attraction between neighboring substitutional Mn atoms and the interstitial impurity decrease this barrier, ultimately resulting in a general decrease of stability with Mn concentration. On the other hand, the thermal stability of **substitutional Mn** atoms determines a maximum annealing temperature at which interstitial out-diffusion can be promoted while maintaining a dilute Mn distribution, i.e. without Mn segregation into secondary phases. Manganese in these compounds diffuses through interstitial sites, which translates directly on their stability on substitutional sites. In other words, a lower interstitial Mn stability also decreases substitutional Mn stability. Moreover, larger Mn contents in III-Mn-V semiconductors result in lower substitutional Mn stability, which can be correlated with an early onset of Mn segregation into secondary phases.

Aimed towards comprehending the interplay between these two effects, the emission channeling experiments performed in (Ga,Mn)As films described in this thesis estimated activation energies for diffusion of interstitial Mn at 1.6 – 2.0 eV for 1% and 1.3 – 1.6 eV for 5% Mn, and of substitutional Mn at

2.4 eV and 1.9 eV, respectively. This represents a significant decrease from the experiments in the ultra-low concentration regime in GaAs, with activation energies of 1.7 – 2.3 eV for interstitial diffusion and 2.3 eV for substitutional.

The investigation of lattice location and thermal stability of Mn dopants has also been extended to other III-V systems: in the ultra-dilute regime in GaP, GaAs and GaSb, and at higher Mn concentrations, particularly in (Ga,Mn)Sb and quaternary (Ga,Mn)(As,X), with X=(P,Sb). In the ultra dilute concentration regime ($x_{\text{Mn}} < 0.05\%$), a decreasing activation energy for diffusion for both substitutional and interstitial Mn reflects the incorporation of heavier group V element, observed in the emission channeling experiments in GaP, GaAs and GaSb. Particularly, the activation energy for substitutional diffusion changes from > 3.4 eV to 3.0 eV to > 2.4 eV, for GaP, GaAs and GaSb, respectively, while for the interstitial diffusion from 2.0 – 2.8 eV to 1.7 – 2.3 eV to 1.0 – 1.4 eV. This directly results from the decreasing bond strength between Ga and the group V element X: as X becomes heavier, the bond strength typically becomes smaller, increasing the crystal lattice constant, dielectric constant and also decreasing the semiconductor's band-gap.

The same trend has been observed in III-Mn-V dilute magnetic semiconductors, where the Mn thermal stability decreases as composition is changed from phosphorus to arsenic to antimony. This decrease is, however, not only connected with the bonding between Ga and the Group V element, but also with the larger Mn contents which directly influences interstitial Mn stability. Doping (Ga,Mn)As layers with phosphorous (P) increases the stability of both substitutional and interstitial Mn atoms, slowing Mn_i out-diffusion while reducing substitutional segregation. On the other hand, antimony doping has little effect on the Mn thermal stability of (Ga,Mn)(As,Sb) layers when compared to (Ga,Mn)As, possibly due to low Sb doping (10%). It has been shown elsewhere that Sb doping greatly decreases crystalline quality, limiting its incorporation towards higher concentrations. As-grown Sb-doped (Ga,Mn)As films showed similar effective magnetization as (Ga,Mn)As grown under similar conditions. However, the thermal stability of Mn atoms is significantly different for (Ga,Mn)Sb layers, where interstitial Mn becomes mobile and substitutional Mn unstable at lower temperatures than (Ga,Mn)As. While the larger interstitial

mobility translates into Mn being removed at growth temperatures, and thus little magnetic compensation present in as-grown films, the lower stability of substitutional Mn leads to the formation of secondary phases. Consequently, it remains a challenge to grow dilute (Ga,Mn)Sb layers, without the presence of MnSb and MnAs secondary phases.

Annealing III-Mn-V layers at higher temperatures typically results in a variety of different phases, which were particularly investigated in (Ga,Mn)As films. At temperatures close to the growth temperature, this procedure has been observed to increase ferromagnetic Curie temperature due to the interstitial out-diffusion. Annealing at (slightly) higher temperatures promotes the segregation of Mn, forming hybrid phases with MnAs nanoclusters embedded in a GaAs:Mn matrix. The structure and magnetism of these different phases were investigated in (Ga,Mn)As thin films doped with 1% and 5% for select thermal annealing treatments: both before and after interstitial-removing annealing at 200°C, at a previously unreported intermediate annealing step at 300°C, and at a high annealing temperature, 600°C, typical for the formation of MnAs secondary phases. This investigation confirms current understanding of T_C optimization and secondary phase segregation in (Ga,Mn)As through three main results: (i) Mn dopants only stabilize in interstitial positions for the higher concentration, (ii) low temperature annealing increases Curie temperature and magnetization, and (iii) high annealing temperatures lead to segregation into MnAs nanoclusters. The first result (i) is illustrated by the little to no structural and magnetic difference before and after thermal annealing at 200°C for a Mn concentration of 1%. This is in contrast with the second result (ii), at 5% Mn, where a significant increase in magnetization and T_C is observed after thermal annealing, resulting from the partial passivation of interstitial Mn. The third result (iii) also confirmed the presence of MnAs nanoclusters after a thermal annealing treatment at 600°C, with different crystalline structures: *zincblende* and *NiAs-type*. Lastly, this investigation also observed paramagnetic Mn-rich nanoclusters in (Ga,Mn)As annealed at 300°C. This segregation at low-temperature is tied in with the decrease in thermal stability of Mn substitutional dopants, and represents a limiting factor for T_C optimization in (Ga,Mn)As.

In summary, the thermal stability of Mn dopants plays a paramount role in the

structure and magnetism of III-Mn-V ferromagnetic semiconductors. Achieving higher Curie temperatures in these compounds through thermal annealing involves a complex balance between out-diffusion of compensating interstitials and segregation of substitutional Mn.

The second part of this thesis focused on the lattice location of Mn in **multiferroic Rashba semiconductor** (Ge,Mn)Te, which allowed for an assessment of the Mn sub-lattice displacement in the ferroelectric phase, providing insight into its role on the material multiferroic properties. The Mn sub-lattice displacement experienced by implanted ^{56}Mn radioactive probes in GeTe and (Ge,Mn)Te crystals was measured at 100 K, well within the ferroelectric phase, at Mn concentrations of 13%, 16%, 20% and 21%, and was found to slightly decrease from $0.19 \pm 0.02 \text{ \AA}$ in GeTe (0% Mn) to $0.14 \pm 0.02 \text{ \AA}$ in (Ge,Mn)Te (21% Mn). Additionally, the direction and orientation of the Mn sub-lattice displacement was also determined to predominantly follow the substrate $\langle 111 \rangle$ out-of-surface direction within the probed Mn concentration range. This is in good agreement with the preferential orientation of ferroelectric domains along the $\langle 111 \rangle$ out-of-surface direction observed in (Ge,Mn)Te films with Mn concentrations up to $x_{\text{Mn}} \sim 0.2$.^{34,129} Above this threshold, the rhombohedral distortion angle becomes negligible, and other oblique [111] crystalline axes become equivalent to the off-surface [111] axis. This has a strong impact on the orientation of different crystallites in (Ge,Mn)Te, which have equal populations at concentrations above $x_{\text{Mn}} \sim 0.2$, and actively change the orientations of both ferroelectric polarization and ferromagnetic anisotropy.³⁴ Our emission channeling experiments were not designed to quantify this effect, but are still sensitive to changes in the crystalline structure, which were indeed observed for measurements performed on (Ge,Mn)Te with a 21% Mn content. The direct evidence for the Mn sub-lattice displacement magnitude and direction contributes towards the comprehensive understanding of the interplay between ferroelectric polarization and ferromagnetic magnetization directions, which ultimately drives the magnetoelectric coupling in (Ge,Mn)Te. Below $x_{\text{Mn}} \sim 0.20$ content, the rhombohedral distortion plays an important role in pinning both the **FE** and **FM** directions, allowing for an all electric control of magnetization and ferroelectric polarization,³³ and opening the path towards

further functionalization of MUFERS.

10.1 Outlook

From a more fundamental point of view, the main implications of the results presented in this thesis concern the understanding of the lattice location of magnetic dopants in ferromagnetic semiconductors and provide insight on their role both in the macroscopic properties and in the functionalization of ferromagnetic semiconductors. The balance between the thermal stability of interstitial and substitutional dopants in III-Mn-V dilute magnetic semiconductors not only directly influences the magnetization and maximum Curie temperature achievable in these systems, but also increases the complexity degree of their synthesis and post-processing. In multiferroic Rashba semiconductor (Ge,Mn)Te, the rhombohedral distortion induces a preferential ferroelectric polarization direction, associated with the displacement between Ge and Te sub-lattices. It also modulates the displacement of the Mn dopants sub-lattice, influencing the magnetization direction and coupling it with the ferroelectric polarization, resulting in an electric- and magnetic-field tunable multiferroic system.^{33,34}

On an individual level the results discussed in this thesis motivate further investigation into the fundamental mechanisms behind local structure of Mn dopants in ferromagnetic semiconductors. On the theoretical side, first principles calculations could provide insight on two fronts: (i) on the formation and thermal stability of Mn impurities in III-Mn-V semiconductors, and (ii) on the displacement of Mn sub-lattice in (Ge,Mn)Te crystals, taking into account substrate interactions. The first would greatly benefit the understanding of Mn stabilization in anion-substitutional sites, particularly in GaP and GaN semiconductors, as well as possibly clarify which mechanisms limit the diffusion of both interstitial and Ga-substitutional Mn atoms in Mn-doped semiconductors. The second could not only settle the disparity between the results presented in this thesis and literature values for the displacement of Mn sub-lattice in (Ge,Mn)Te, but also unveil the mechanism behind the unidirectionality of the

ferroelectric polarization in this material. On the experimental side, since MUFERS have been far less investigated than DMS materials, more pathways remain for furthering the understanding of their structural, ferroelectric and ferromagnetic properties. Nevertheless, for dilute magnetic semiconductors such as (Ga,Mn)As, our results inspire may inspire new approaches to achieving higher Curie temperatures, for example, combining ion-irradiation and thermal annealing to increasing effective substitutional incorporation.

Multiferroic Rashba semiconductors, on the other hand, are a recent topic which is still gaining momentum, with Mn-doped GeTe at its vanguard. In particular, the results described in this thesis focused on the displacement of the Mn dopant sub-lattice, situating it at smaller values than the Ge sub-lattice. Yet, it remains ambiguous how the Ge sub-lattice displacement changes with increasing Mn contents in (Ge,Mn)Te layers, as well as its role on the magnetoelectric coupling above 20% Mn. A direct assessment of this displacement could be performed by lattice location experiments using different ion-beam analysis techniques, such Rutherford backscattering spectroscopy (RBS) and particle induced x-ray emission (PIXE). In particular, this investigation could be performed through the acquisition of two-dimensional channeling patterns and an analysis similar to the emission channeling methodology, by fitting with theoretical simulations. Moreover, this assessment could be further extended through the direct measurement of the sub-lattice displacement within the multiferroic phase. Of particular interest would be to be able to observe and quantify the change in both Ge and Mn sub-lattices upon ferromagnetic (ferroelectric) switching through magnetoelectric coupling, by *in-situ* application of electric (magnetic) fields.

From a different perspective, first principles studies have predicted that doping with other transition metals and/or semi-metals can add further tunability to GeTe layers, e.g. to increase Curie temperature. Furthermore, doping with a few percent of semi-metals, such as Sn, has been shown to decrease the rhombohedral distortion of GeTe layers, while maintaining a significant ferroelectric polarization, i.e. providing an additional means to tune the multiferroicity and the associated Rashba and Zeeman effects.

In conclusion, a deeper fundamental understanding of the lattice location and

thermal stability of dopants and impurities in ferromagnetic semiconductors paves the way towards a higher degree of tunability of their macroscopic properties.

“To raise new questions, new possibilities, to regard old problems from a new angle, requires creative imagination and marks real advance in science.”

Albert Einstein, *The Evolution of Physics* (1961)²⁴⁷

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- Erasmus Placement at Gent Universiteit, Belgium
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Experience

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SCIENTIFIC RESEARCHER

Nov. 2014 - PRESENT

- Expert on thin film characterization using Ion Beam Analysis and Emission Channeling techniques
- Collaboration with large-scale facilities such as CERN (Switzerland and ESRF (France)

Languages

Professional proficiency Portuguese, English

Basic proficiency Spanish, Dutch, French, Russian

Extracurricular Activity

APEI Benelux

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Co-FOUNDER & VICE-PRESIDENT

Nov. 2016 - PRESENT

- Gained expertise and strengthened networking, team-building, event organizing and leadership skills
- Organized national and international events with participation of governmental representatives (EU Parliament and Portuguese Government)

IFIMUP-IN

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COMPUTATIONAL TRAINEE

Mar. 2011 - Sep. 2012

- Developed computational models for localized magnetic refrigeration using operational COMSOL Multiphysics
- Developed a heat transfer measurement system

Hobbies

Low-end practice (Bass) · Latin Dances · Scuba diving · High Intensity Interval Training · Social events

Honors & Awards

2018 **Best Young Speaker Award**, ISOLDE Workshop and Users Meeting 2018, CERN

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Publications

- V. Augustyns *et al.* (2017). "Evidence of tetragonal distortion as the origin of the ferromagnetic ground state in gamma-Fe nanoparticles"
In: *Physical Review B* 96. ARTN 174410 (17). ISSN: 2469-9950
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