Magnetic coupling in (GaMn)As ferromagnetic semiconductors - studied by soft x-ray spectroscopy

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Chapter 1

Introduction

derromagnetic semiconductors a new material class designed for spintronic applications

The term ”spintronics” refers to electronic devices that utilize not only the charge of the carriers but also their magnetic moment the so called spin. The huge potential of this combination was impressively demonstrated by the discovery of the giant magneto resistance (GMR) effect in 1988. The GMR effect exploits the spin dependent scattering of conduction electrons in a structure of two ferromagnetic layers separated by a non magnetic spacer layer [75, 76]. Depending on its magnetic direction, a single-domain magnetic material will scatter electrons with ”up” or ”down” spin differently. Thus electrons become spin polarized if they pass through a magnetic layer. When the two magnetic layers in GMR structures are aligned anti-parallel, the resistivity is high because conduction electrons polarized by the first magnetic layer will find a reversed magnetization direction if they enter the second magnetic layer and undergo additional spin-flip scattering [76]. When the layers are aligned in parallel less spin flip scattering occurs, yielding a lower resistance of the GMR structure [76]. Today the effect is widely used in magnetic sensors and read heads for hard drives. It is a prominent example for the benefit of industrial applications from fundamental research. The interest to incorporate such effects in integrated circuits, e.g. as magneto resistive random access memory devices, is huge. But the implementation is hampered by the choice of the right material. Electronic devices are mainly made of semiconductors whereas only transition metals or rare earth metals show ferromagnetism e.g. spontaneous magnetic ordering with a net spin polarization. It is rather difficult to combine these two material classes in functional heterostructures [77]. On the one hand metal films can not easily be integrated in the production process of semiconductor plants on the other hand the injection of spin polarized carriers across a metal-semiconductor interface is rather inefficient. The large difference in the density of states and the resulting band structure will cause scattering at the interface that destroys the spin polarization [77].
This explains why the discovery of ferromagnetism in $III - V$ and $II - VI$ dilute magnetic semiconductors (DMS) attracted such a large interest. These systems are promising candidates for spintronic devices since the above described interface problem is avoided in a very elegant way. Spin polarized carriers are provided by magnetic ions integrated in the semiconductor host matrix. Experiments performed on DMS so far show new and fascinating physical properties that have not been observed in other systems yet. It has been demonstrated that the magnetic properties can be changed isothermally by light or electric fields in $(In,Mn)As/(Al,Ga)Sb$ heterostructures [30]. The anisotropy in $Ga_{1-x}Mn_xAs$ can be tailored by the choice of temperature and carrier concentration [54]. Also spin injection from $Ga_{1-x}Mn_xAs$ into a $(InGa)As$ has been demonstrated. Unfortunately up to now all dilute magnetic semiconductor materials suffer from a Curie temperature far below room temperature. At the moment the world record Curie temperature for $Ga_{1-x}Mn_xAs$ is at $173K$ [83]. But nevertheless these materials are an ideal test ground to study the interplay of quantization effects, magnetism, carrier dynamics and transport properties. The prospects of spintronic devices that allow to incorporate data processing and storage in a single chip is more than encouraging. Thus the community investigating the magnetic properties of DMS’s is steadily growing.

In this thesis the origin of the ferromagnetic ordering in $Ga_{1-x}Mn_xAs$, the most prominent member of the $III - V$ series of ferromagnetic DMS, is investigated by x-ray spectroscopy (XAS) in combination with x-ray magnetic circular dichroism (XMCD). The ferromagnetism in $(Ga_{1-x}Mn_x)As$ is based on two cooperative effects caused by replacing the trivalent Ga atoms with Mn. Mn provides a local spin magnetic moment and as an acceptor it creates itinerant holes, which mediate the long range ferromagnetic order [1]. But despite the existence of various theoretical models the physics underlying the magnetic properties is still under discussion [2, 3]. This is partially due to the high degree of disorder in these systems caused by the limited solubility of Mn. The formation of As antisites and interstitial Mn were predicted [4]. Both defects act as double donors partially compensating the effect of the Mn acceptors [4]. For the understanding of the ferromagnetic ordering the electronic configuration of the Mn impurities and the number of Mn atoms contributing to the long range ferromagnetic order are of major interest. These parameters can be probed directly by x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD). At the Mn $2p - 3d$ resonance the XAS and MXCD line shapes are characteristic for the Mn $3d$ electronic and magnetic ground state configuration respectively [51]. This is a major advantage of the x-ray spectroscopy compared to the widely used SQUID measurements.

This work starts with a short introduction to the principles of x-ray absorption spectroscopy. In the following chapter we give an overview on the various theoretical models describing the origin of ferromagnetic coupling in $Ga_{1-x}Mn_xAs$. After presenting the experimental details the chemical and magnetic depth profiles of
different $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ layers are investigated. The main question at this point is the diffusion of interstitial Mn during the growth and annealing process and its influence on the ferromagnetic coupling. The signature of Mn $3d^5$-$3d^6$ mixed valence acceptor states responsible for long-range ferromagnetic order is identified with x-ray magnetic circular dichroism at all Mn concentrations. In chapter 6 we demonstrate that an additional non-ferromagnetic Mn species with an electron count close to $3d^4$ is observed at high Mn concentrations. We discuss a model in which the latter is due to Mn-Mn antiferromagnetic nearest neighbor pairs. The last chapter deals with the orbital magnetic moment anisotropy present in $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ films. The microscopic origin of the orbital magnetic moment anisotropy is probed by x-ray magnetic circular dichroism spectroscopy. It provides first evidence for an anisotropic $pd$-hybridization and, therefore, anisotropic exchange coupling.
Introduction
Chapter 2

Soft x-ray absorption spectroscopy

The fundamental interactions of x-rays with matter are the photoelectric absorption, scattering processes like Thompson (elastic) and Compton (inelastic) scattering and the formation of electron positron pairs (above a threshold of 1,022 MeV photon energy). In the regime of soft x-rays (below 10\(keV\) photon energy) the cross section of photoelectric absorption is two to three orders of magnitude larger than that of the scattering processes. This effect refers to the absorption of an incoming photon by a core electron exciting the electron to a bound state or into the continuum if the photon energy is higher than the binding energy and the work function of the solid. The photoelectric effect was discovered by Heinrich Hertz in 1887 and could not be explained within the classical theory at this time. Albert Einstein succeeded to explain the photoelectric effect by the quantum nature of light and received in 1921 the Nobel price for his findings. Today the photoelectric effect is one of the most popular tools to study the electronic structure in solid state and surface science. Measuring the x-ray absorption coefficient as a function of photon energy near the absorption edge of the element of interest is a widely used technique to obtain information on the chemical environment of the probed element, its valency, its spin state and so on. Synchrotron sources like BESSY provide soft x-rays at high brilliance, an energy resolution below 0.2\(eV\) and with full polarization control. The latter is especially important for the analysis of magnetic samples by x-ray spectroscopy. Similar to the Faraday-Kerr effect in the optical regime, the x-ray absorption coefficient for polarized x-rays depends on the magnetization vector which also allows to study magnetic properties by x-ray spectroscopy. The most popular effect is the x-ray magnetic circular dichroism (XMCD) i.e. the difference of the x-ray absorption coefficient between two helicities of a circular polarized incident photon beam. The combination of x-ray absorption spectroscopy and x-ray magnetic circular dichroism is ideally suited to study the 3\(d\) shell of transition metals like Ni or Mn since electronic configuration and magnetic moments can be investigated
simultaneously.

### 2.1 The dipole transition

The absorption cross section $\sigma$ is defined as the number of excited electrons per time unit divided by the photon flux $I_{ph}$:

$$\sigma(E) = \frac{\sum_{i,f} W_{i\rightarrow f}}{I_{ph}}$$  \hspace{1cm} (2.1)

Whereby $W_{i\rightarrow f}$ denotes the probability per unit time to promote a core electron from the initial state $|i>\rangle$ into the final state $|f<\rangle$ by the absorption of a photon of the energy $E = \hbar \omega$. This transition probability is given by Fermi’s golden rule. It describes the transition probability from the initial state $|i>\rangle$ in to the final state $|f<\rangle$ under the influence of the perturbation $H'$ as

$$W_{i\rightarrow f} = \frac{2\pi}{\hbar} |<f|H'|i>|^2 \delta(E_f - E_i - \hbar \omega).$$  \hspace{1cm} (2.2)

The $\delta$-function represents the energy conservation; transitions are only possible if the energy interval between initial and final state corresponds to the energy of the absorbed photon. The electromagnetic field of the photons can be described by the vector potential $A(r,t) = A_0 e^{i(ky - \omega t)}$ in terms of an electromagnetic plane wave. With the wave vector $k$, frequency $\omega$ and the polarization vector $\varepsilon$. $e^0$ corresponds to linear and $e^{-1}$ ($e^{+1}$) to left (right) circular polarization with a polarization vector $\varepsilon^{+1} = 1/\sqrt{2}(\varepsilon_x + i\varepsilon_y)$ ($\varepsilon^{-1} = 1/\sqrt{2}(\varepsilon_x - i\varepsilon_y)$). Circular polarized photons carry an angular momentum which is parallel (antiparallel) to the wave vector $k$ for left (right) circular polarization. The Hamiltonian becomes [38]

$$H = \frac{1}{2m}[P - e\varepsilon A(r,t)]^2 + V(r) - \frac{e}{mc} S \cdot (\nabla \times A(r,t)).$$  \hspace{1cm} (2.3)

The last term describes the interaction of the magnetic moment of the electrons with the oscillating field of the electromagnetic wave. A decomposition in the undisturbed Hamiltonian of the atom and the perturbation results in:

$$H = H_0 - \frac{e}{mc} \underbrace{P \cdot A(r,t)}_{H_I} - \frac{e}{mc} \underbrace{S \cdot (\nabla \times A(r,t))}_{H_{II}} + \frac{e^2}{2mc^2} \underbrace{A^2(r,t)}_{H_{III}}$$  \hspace{1cm} (2.4)

In a first order approximation the term quadratic in $A$ can be neglected. The matrix elements of term $II$ are in the order of $\hbar \cdot k A_0$ and compare to those of the term $I$ like the impulse if the absorbed photon to the momentum of the electron:

$$\frac{H_{II}}{H_I} \approx \frac{\hbar k}{p} \ll 1.$$  \hspace{1cm} (2.5)
2.1 The dipole transition

In the energy range below 1000 eV that we are interested in the momentum of the photon can be neglected. In this approximation the transition probability can be expressed by a dipole transition:

\[
W_{i\rightarrow f} = \frac{2\pi}{\hbar} \frac{e}{mc} |< f| \mathbf{A} \cdot \mathbf{P} |i>|^2 \delta(E_f - E_i - \hbar\omega).
\]  

(2.6)

According to the Wigner-Eckart theorem the dipole selection rules for linear polarized light are:

\[
\Delta j = 0, \pm 1; \; \Delta l = \pm 1; \; \Delta m = 0; \; \Delta s = 0.
\]  

(2.7)

And for circular polarized light:

\[
\Delta j = 0, \pm 1; \; \Delta l = \pm 1; \; \Delta m = \pm 1; \; \Delta s = 0.
\]  

(2.8)

By the selection rules we find that the dipole transitions are spin conservative and orbital selective as \(\Delta m\) is determined by the polarization of the photon \((\Delta m = 1 (-1)\) for left circular (right circular) polarization. The total absorption cross section in the dipole approximation is given by the sum of all initial and final states. With the incident photon flux written as the energy flux of the electromagnetic field divided by the photon energy \(I_{ph} = \frac{E_{ph}^2}{2\pi\hbar\omega} = \frac{A_{ph}^2}{2\pi\hbar c}\), the photoabsorption cross section in the dipole approximation reads:

\[
\sigma(\hbar\omega) = 4\pi^2 \alpha \hbar\omega \sum_{i,f} |< f| \mathbf{r} |i>|^2 \delta(E_f - E_i - \hbar\omega).
\]  

(2.9)

Whereby \(\alpha\) is the fine structure constant \((\alpha = 1/137)\). The electronic and magnetic properties of the transition metals are determined by the occupation of the 3d shell. Such they are ideally accessible to soft x-ray spectroscopy at the 2p–3d resonance. But the conservation of orbital angular momentum \((\Delta l = \pm 1)\) allows transitions from the 2p level into 3d as well as into 4s states. The absorption cross section that we measure at the 2p–3d resonance is, therefore, a mixture of two transition channels as shown in Fig. 2.1. Transitions into continuum 4s states cause a step like background whereas the intensity of the resonance peaks in the absorption spectrum is proportional to the unoccupied 3d states.

### 2.1.1 X-ray magnetic circular dichroism

The x-ray magnetic circular dichroism (XMCD) is defined as the difference in the absorption cross section between left and right circularly polarized x-ray light with the wave vector \(\mathbf{k}\) parallel to the magnetization \(\mathbf{M}\) (the x-ray helicity \(\epsilon^\pm\) is collinear with the propagation direction). This effect is the analogue to the magneto optical Faraday effect in the soft x-ray regime. In 1845 Faraday discovered a rotation of the polarization vector of linearly polarized light upon
Figure 2.1: X-ray absorption spectra recorded at the Mn L\textsubscript{3} / L\textsubscript{2} edges of a Ga\textsubscript{1-x}Mn\textsubscript{x}As sample. The resonance peaks are due to transitions in unoccupied 3d levels as indicated by the inset. Transition into continuum states (represented by the parabola) cause a step-like background.
2.1 The dipole transition

the transmission through silicon borate in an applied magnetic field. Due to
the exchange split valence states the absorption coefficient for the two circular
components of the incident light is different. This effect also causes a rotation
of the linear polarization into elliptically polarized light after the transmission.

The XMCD effect occurring at the L₃ and L₂ edge of 3d transition metals
can be explained within a qualitative picture. The circular polarized photon gets
absorbed generating a hole in the 2p shell. The p states are split into the 2p₃/₂
and 2p₁/₂ level by the spin orbit interaction. This interaction couples the spin of
the 2p electrons to the orbital moment. At the 2p₃/₂ and the 2p₁/₂ level the orbital
angular momentum l and the spin angular momentum s are coupled parallel and
antiparallel, respectively. The spin-orbit coupling allows to excite electrons of
the 2p shell by circular polarized light spin selective into the valence shell even if
the dipole operator does not act on the spin. The spin polarization arises from
the selection rule for the orbital magnetic moment depending on the polarization
on the absorbed x-ray photon. Because of the parallel coupling of l and s at the
2p₃/₂ level and the antiparallel at the 2p₁/₂ level, transitions from the 2p₃/₂ and
the 2p₁/₂ levels into the valence shell occur with different spin polarization.

Possible final states for the photoexcitation are the unoccupied 3d and 4s
states above the Fermi level. The dipole transition is spin conservative which
means that and spin up electron can only be promoted in to a spin up empty
state and vice versa. In a ferromagnetic transition metal there is an imbalance
of unoccupied spin-up and spin-down states in the d-band due to the exchange
coupling (Stoner model). If the orientation of the magnetization M is parallel to
the photon wave vector k this imbalance of empty d-states leads to a spin selec-
tive excitation process, i.e. the probability of an electron transition excited by a
circular polarized photon is proportional to the unoccupied d-states. It causes an
asymmetry in the absorption cross sections for left and right circular polarized
light which is proportional to the difference in the unoccupied spin-up and spin-
down states, i.e. the spin magnetic moment. But the photoelectron also probes
the orbital magnetic moment of the valence band. Due to the conservation of
angular momentum the change in the quantum number m is determined by the
polarization of the photon. Left circular polarized photons with the magnetic
moment +ℏ can cause only transitions with Δm = 1 and accordingly right circular
polarized photons can cause only transitions with Δm = −1. If the valence
states with quantum numbers ±m_l are unequally occupied the absorption of pho-
tons with opposite helicity will be different. An example of the XMCD effect is
given in Fig. 2.2. For a magnetically almost saturated Ga₁₋ₓMnxAs sample at
10K we find a huge difference between the absorption spectra recorded with left
and right circular polarized x-rays. The XMCD signal changes sign between the
L₃ and L₂ edge because of the parallel and antiparallel coupling of l and s at the
2p₁/₂ and 2p₃/₂ levels, respectively.
Figure 2.2: The upper panel displays x-ray absorption spectra recorded at the Mn $2p - 3d$ resonance exciting with left (blue line) and right (red line) circular polarized x-rays. The sample was a Ga$_{1-x}$Mn$_x$As ($x=0.017$) at 10K and in 4T external magnetic field. A schematic picture of the absorption process is given in the inset. The lower panel shows the XMCD spectrum (difference spectrum).
2.2 Analysis of XAS and XMCD spectra

2.2.1 Sum rules

The sum rules allow under certain approximations to extract from the XAS and XMCD spectra quantitative information on the ground state spin and orbital magnetic moments of the atomic shell into which the core electron is excited. The sum rules presented here were derived for dipole transitions from the levels $j^\pm = c \pm 1/2$ of the spin-orbit splitted core state $c$ towards a valence level $l$ with $n$ electrons [58]. The first sum rule was derived by Thole et al. [58]. It states that the integral over the XMCD signal (the difference in the absorption cross section between left ($\sigma^-$) and right ($\sigma^+$) circularly polarized x-ray light with the wave vector $k$ parallel to the magnetization $M$) normalized to the integral over the unpolarized absorption cross section is proportional to the average expectation value of the orbital momentum operator $L_z$ acting on the shell in which the photoelectron is excited [58].

$$\frac{\int_{j+} \sigma^+ - \sigma^- d\omega}{\int_{j+} \sigma^+ + \sigma^- + \sigma^0 d\omega} = \frac{l(l+1) + 2 - c(c+1)}{2l(l+1)(4l+2) - n} < L_z > \quad (2.10)$$

A second sum rule that relates the integrated XMCD signal to the average expectation value of the spin momentum operator $S_z$ was derived by Carra et al. later on [59].

$$\frac{\int_{j+} \sigma^+ - \sigma^- d\omega - \frac{c+1}{c} \int_{j-} \sigma^+ - \sigma^- d\omega}{\int_{j+} \sigma^+ + \sigma^- + \sigma^0 d\omega} = \frac{l(l+1) - 2 - c(c+1)}{3c(4l+2) - n} < S_z > \quad (2.11)$$

$$+ \frac{l(l+1)[l(l+1) + 2c(c+1) + 4] - 3(c-1)^2(c+2)^2}{6lc(l+1)(4l+2) - n} < T_z >$$

Whereby $< T_z >$ is the expectation value of the magnetic dipole operator, which measures the asphericity of the spin magnetization. Such anisotropy can be caused by distortions of the valence shell due to the spin-orbit interaction or the crystal field. It is defined as:

$$\vec{T} = \vec{S} - 3\vec{r} (\vec{r} \times \vec{S})$$

In principle the sum rules are only applicable to a single transition channel. Whereas the spectra recorded at the $2p - 3d$ resonance also contain contributions from transitions into $4s$ states. Such a mixture of transition channels contributing to the XMCD spectra is problematic for the application of the sum rules since the sum rules would be different for the two channels. But fortunately the ratio of the radial dipole matrix elements for the $2p \rightarrow 4s$ and the $2p \rightarrow 3d$ transitions is rather small, and the $2p \rightarrow 4s$ transitions can be neglected.

$$\frac{|<4s||r||2p>|^2}{|<3d||r||2p>|^2} \approx 0.02 \quad (2.13)$$
If we take only the transitions into 3\textit{d} final states (l=2) with the number of holes \( n_{3d} = 4l + 2 - n \) into account the sum rules read [60]:

\[
m_L = \frac{\mu_B}{\hbar} < L_z > = -\frac{4}{3} \int_{L_3+L_2} (\sigma_+ - \sigma_-) d\omega \int_{L_3+L_2} (\sigma_+ + \sigma_-) d\omega (10 - n_{3d}) \quad (2.14)
\]

\[
m_s = \frac{2\mu_B}{\hbar} < S_z > = -\frac{6}{4} \int_{L_3} (\sigma_+ - \sigma_-) d\omega - \frac{4}{\int_{L_3+L_2} (\sigma_+ - \sigma_-) d\omega} \int_{L_3+L_2} (\sigma_+ + \sigma_-) d\omega \int_{L_3} (\sigma_+ + \sigma_-) d\omega (10 - n_{3d})(1 + \frac{7}{2} < T_z >) \quad (2.15)
\]

Whereby the relative cross-section for linearly polarized light, \( \sigma_0 \), was replaced by \( (\sigma_+ + \sigma_-)/2 \). This is justified since usually the x-ray linear magnetic dichroism is much smaller than the XMCD effect [79]. An example for the application of the sum rules is given in Fig. 2.3. It shows the unpolarized absorption spectrum and the XMCD spectrum obtained from a Nickel film. The integrals over the XMCD spectrum and the isotropic spectrum after subtraction of the step like background (to remove the contributions from transitions into continuum states) are indicated by dashed lines. The presence of an orbital moment can be estimated directly from the non vanishing integral over the XMCD spectrum \( \int_{L_3+L_2} \sigma^+ - \sigma^- \). A negative (positive) value corresponds to a parallel (antiparallel) alignment of orbital and spin moment.

For the derivation of the spin sum rule it is assumed that the L\textsubscript{3} and the L\textsubscript{2} edge are well separated. This assumption is only correct if the spin-orbit-splitting of the core hole is large compared to the coulomb interactions between the core hole and the final states that lead to a coupling of the two L\textsubscript{2,3} absorption edges. Such coulomb interactions with the final state affects directly the ratio between the absorption coefficients at the L\textsubscript{3} and the L\textsubscript{2} edge, the so called branching ratio. It was predicted that the intermixing of the L\textsubscript{2} and L\textsubscript{3} absorption edges is mainly present towards the early transition metals [64] where the electron core hole interaction increases while the spin-orbit splitting decreases. For such metals (e.g. Mn) the application of the spin sum rule can produce an error up to 30%. Whereas the determination of the orbital moment by the sum rules is not affected by such intermixing.

A further assumption is that the radial matrix element can be taken as constant due to the normalization to the isotropic absorption cross-section. Wu et al. calculated for Ni that the radial part of the matrix elements of the d band \( |<3d|r|2p>|^2 \) varies linearly with the photon energy by \( \approx 30\% \) and is proportional to the spin-orbit coupling in the 3d shell [63]. Since the dichroic signal is proportional to the radial part of the matrix elements and \( L_z \) is proportional to the spin-orbit coupling in the 3d shell this approximation does not have any effect on the orbital sum rule. Whereas the spin sum rule is affected by the energy dependent radial matrix elements [63]. However the sum rules are normalized
Figure 2.3: Application of the sum rules to Ni XAS and XMCD spectra. The dotted line in the upper panel shows the two step function that was subtracted from the XAS sum spectrum (solid line) prior to the integration to remove the contributions due to transition into continuum states. The integrals that are used for sum rule analysis are indicated by the arrows.
to the isotropic absorption cross-section which is proportional to the number of holes in the d-shell. But also s and p (continuum states) states contribute to the measured absorption cross-section. To eliminate these contributions a double step function is fitted below the absorption cross-section and subtracted as shown in Fig. 2.3. This procedure is likely to introduce a systematic error in the determination of the number of holes in the final state.

It has been shown by ref. [60] that for the transition metals Iron and Cobalt the spin and orbital moments determined by the application of the sum rules are in good agreement with those obtained from Einstein de Haas gyromagnetic ratio measurements.

2.2.2 Multiplet structure

Electronic and magnetic properties of the transition metals are characterized by the 3d states which are successively filled across the series, the Fermi surface is mainly formed by these states. Compared to the sp bands, with almost free electron character, the 3d bands with a bandwidth of $5 - 10$ eV are less itinerant. Coulomb and exchange interaction split the 3d shell into a magnitude of energy levels corresponding to the possible combinations of the orbital and spin quantum numbers $m_l$ and $m_s$ of the residing electrons. The multiplet terms for the different occupation of the 3d shell are shown in Fig. 2.4 (taken from [65]). The lowest energy states can be found at the top of Fig. 2.4. In this ground state configuration the multiplet is occupied according to Hund’s rules. This means that first the spin moment is maximized, then the orbital angular momentum and then both are coupled to lowest (highest) possible total angular momentum for a less (more) than half filled shell [82]. The multiplet terms of the 3d shell have a strong influence on the hybridization and the magnetic coupling of the transition metals. In Nickel for example the hybridization of the 3d-shells of atomic neighbors leads to an admixture of $d^{10}$ and $d^8$ contributions in the ground state configuration [82]. Thus two adjacent Nickel atoms with two holes can have either a

$$d^9 + (\uparrow) + d9 + (\downarrow) \longleftrightarrow d^8 + (\uparrow \downarrow) + d^{10} \tag{2.16}$$

or a

$$d^9 + (\uparrow) + d9 + (\downarrow) \longleftrightarrow d^8 + (\uparrow \uparrow) + d^{10} \tag{2.17}$$

configuration. In Nickel metal it is not the $d^8 + (\uparrow \downarrow)$ singlet state that has the lowest energy but the $d^8 + (\uparrow \uparrow)$ configuration with parallel arrangement of the spins [82]. Thus the electron correlation causes the ferromagnetic spin alignment of adjacent Ni atoms which fluctuate between $d^9 + d^9$ and $d^8 + d^{10}$ [82].

A strong advantage of the x-ray spectroscopy at the L$_{2,3}$ edges is that, provided the experimental resolution is high enough, these multiplet splitting of the 3d shell can be resolved in the $2p - 3d$ absorption spectra. Because of the large Coulomb interaction between the $2p$ and the $3d$ levels the dipole transitions depend strongly
Figure 2.4: Energy distribution of the terms in the initial state configuration $3d^n$. The terms are collected in spin manifolds, where the labels give the values of $2S+1$ and $L$. The lowest energy state is at the top of the diagram. (taken from [65])
on the local electronic structure [82]. Van der Laan et al. used a localized description for the $3d^n$ to $2p^53d^{n+1}$ excitation that includes the $3d$-$3d$ and $2p$-$3d$ Coulomb and exchange interactions, the $2p$ and $3d$ spin-orbit interactions and the crystal field acting on the $3d$ states to calculate the $L_{2,3}$ absorption spectra of different transition metals [51]. It was demonstrated that the multiplet structure at the $L_{2,3}$ edges can act as an fingerprint of a particular electronic ground state configuration of the $3d$-shell [52]. For the case of Nickel experimental XAS and XMCD spectra are displayed in Fig. 2.3. XAS and XMCD lineshapes are dominated by the $d^9 \rightarrow 2p^53d^{10}$ transitions. But due to the $d^8$ admixture in the Ni ground state configuration also $d^8 \rightarrow 2p^53d^9$ transitions should contribute. It has been demonstrated that those transitions cause the satellite structure in the XMCD signal at $\approx 3.3$eV above the $L_3$ peak [72].

Also the XAS branching ratio, $BR = \frac{I_{L_3}}{I_{L_2}} \sigma^0$, is strongly influenced by the interactions in the $3d$ shell. In absence of spin-orbit coupling and electrostatic interactions between core hole and valence electrons on the final state the branching ratio would be statistical, $BR=2/3$, as expected from the quantum degeneracy $2j + 1$ of the $2p$ level. Besides a systematic change in the branching ratio for less than half filled $3d$-shells, it has been shown that a branching ratio larger than the statistical value is typical for high spin states [65]. Depositing Mn on Cu(110) it has been demonstrated that the multiplet structure and the branching ratio in the Mn $2p - 3d$ absorption spectra change with the atomic coordination [50]. At low coverage detailed multiplet structures are visible which are characteristic for an atomiclike $d^5$ ground state accompanied by a large branching ratio of 0.8 [50]. With increasing Mn coverage up to 4 monolayers the XAS spectrum becomes smoother and the XAS spectrum approaches the statistical value of 2/3 [50]. Thus in transition metals we can study the hybridization of the $3d$ shell and its ground state configuration by analyzing the multiplet structure and the branching ratio of the $2p - 3d$ XAS spectra.
Chapter 3

Ferromagnetism in dilute magnetic semiconductors

3.1 Introduction

Magnetic ordering is a result of the interplay between the Coulomb interaction and exchange interaction due to the Pauli principle. A simple model demonstrating this effect is given by Heitler and London for the $H_2$ molecule with two electrons. In this molecule the exchange interaction favors ferromagnetic coupling whereas the kinetic energy is favored in antiferromagnetic coupling. When both spins are parallel the electrons are localized at one atom each and can not jump to the neighboring site. Such antibonding state is energetically not favored. The configuration with the lowest energy is the bonding state with antiferromagnetic coupling. But delocalization of electrons does not generally lead to antiferromagnetic coupling. The coupling of magnetic moments by hybridization depends strongly on the electronic and magnetic ground state which is shown for the transition metals in Fig. 2.4. In the already mentioned case of Nickel, for instance, the hybridization of the $d$-shells between atomic neighbors leads to an admixture of $d^{10}$ and $d^8$ contributions in the otherwise $3d^9$ ground state configuration. The $d^8$ state with the lowest energy is a $^3F$ configuration with parallel arrangement of spins that causes a ferromagnetic coupling between adjacent Nickel atoms [82].

Itinerant metals require approximations to model the spin-spin interactions. A relatively simple approach to handle the spin-spin interactions in solids with itinerant spins is the mean field approximation. It is based on the phenomenological assumption that the elusive spin-spin interaction between electrons can be replaced by the interaction of the spins with a very strong magnetic field. The molecular field will tend to line up the magnetic moments. In such models e.g. the Stoner model ferromagnetism is described as an extreme case of paramagnetism.

So far we considered only the case of direct exchange interaction, where the orbital in which the magnetic moments reside overlap. If direct exchange is
not possible, e.g. the magnetic orbitals are separated too far from each other to overlap, the magnetic moments are able to sustain magnetic interactions via exchange interactions mediated by conduction electrons or valence holes. This indirect exchange coupling is responsible for the magnetism in the rare earth metals, the interlayer exchange coupling in GMR systems or the magnetism in semiconductors doped by transition metals. For the latter we will discuss the possible coupling mechanisms in detail.

3.2 Magnetic ordering in dilute magnetic semiconductors

The magnetic coupling of Mn ions in different types of semiconductors has been studied extensively in the recent years. In II-VI host materials, like ZnTe, Mn is divalent and assumes a $d^5$ high spin configuration ($S=5/2$) [43]. Since the Mn doping in II-VI host materials does not introduce any carriers, the intrinsic carrier density is rather low and the localized Mn spins order paramagnetically. Antiferromagnetic coupling between Mn nearest neighbors, due to short range antiferromagnetic super exchange interactions, has been observed [73]. For highly p-doped Zn$_{1-x}$Mn$_x$Te also carrier mediated ferromagnetic interactions between the Mn magnetic moments have been found [73].

In III-V host materials like GaAs where the Mn replaces trivalent Ga atoms it can be present either in a $d^4$ configuration or a $d^5$ configuration with a weakly bound hole, h. In GaAs it is commonly agreed that Mn is present in a $d^5 + h$ configuration providing not only localized spins but also acting as an acceptor [1]. The $pd$-hybridization of the Mn 3$d$ shell with the dangling bonds of As neighbors induces a spin dependent coupling between the localized Mn spins and the holes [43]. The mobility of holes in the p-doped Ga$_{1-x}$Mn$_x$As changes strongly with the Mn concentration, as the system undergoes a metal to insulator transition (MIT). Impurity bands start to occur at Mn concentrations of $x = 0.01 - 0.02$ [43]. The interest to find a theoretical description of the ferromagnetism in Ga$_{1-x}$Mn$_x$As, which occurs on both sides of the MIT, is huge (especially the calculation of $T_c$). But however, there is no consensus on a common model yet. In the following sections we give a short overview over the different models in literature, describing the ferromagnetic ordering in Ga$_{1-x}$Mn$_x$As.

3.2.1 Zener model

In the metallic regime attempts have been made to describe the ferromagnetism by the Zener model [43]. Zener first proposed this model of ferromagnetism driven by the local exchange coupling between carriers and localized spins. According to the model, polarization of localized spins leads to band splitting. In this spin split band structure carriers become spin polarized to lower their free
3.2 Magnetic ordering in dilute magnetic semiconductors

energy. At sufficiently low temperature the lowering of the free energy overcompensates the energy that is necessary to polarize the localized spins. Below that temperature the ferromagnetic alignment becomes energetically more favorable. For the description of ferromagnetism in metals the Zener model has been abandoned because it does not include the quantum oscillations of the carrier spin polarization around localized spins (Friedel oscillations). For the description of ferromagnetism in dilute magnetic semiconductors the Zener mean field theory has been reconsidered. In Ga$_{1-x}$Mn$_x$As the carrier concentration is often found to be significantly lower than the Mn concentration; in that case oscillations in the carrier spin polarization can be neglected. Within these limitations the Zener mean field theory has been successfully used to describe the $T_c$ in dilute magnetic semiconductors [43] as a function of the Mn concentration, $x$, and the carrier density, $p$. The results of these calculations indicate that the Curie temperature of Ga$_{1-x}$Mn$_x$As should scale with the number of substitutional Mn atoms and the number of carriers like $T_c \propto x \cdot p^{1/3}$. This led to a large experimental effort devoted to increasing the hole density, which is usually much smaller than $x$ due to compensation effects. But more recent calculations [41], taking explicitly into account spatial disorder and a finite mean free path in RKKY theory, showed that this simple relation between $T_c$ and the carrier density will not hold for high carrier densities when $p$ is of the order of $x$. In that case the oscillatory character of the RKKY coupling can no longer be neglected and will cause magnetic frustration limiting $T_c$. The authors also consider the adverse effect of antiferromagnetic exchange between Mn-Mn nearest neighbors on $T_c$.

3.2.2 RKKY coupling

The most prominent type of indirect exchange is known as the RKKY interaction, named after the people who developed this theory (Ruderman, Kittel, Kasuya and Yosida). The basic idea behind this mechanism is that the interaction of carriers and localized magnetic moments will establish a non uniform spin density that leads to an oscillatory behavior of the coupling. For $p$-$d$ hybridization, like in Ga$_{1-x}$Mn$_x$As, the sign of the interaction between magnetic impurities and valence band carriers is typically antiferromagnetic, as the carriers attempt to screen the spin of the impurity. Rather than forming a negative spin -5/2 at the impurity site, the holes instead spin-polarize in concentric rings around the impurity. The source of the rings of alternating polarization is that a true delta-function in space would require, in Fourier k-space, all the k-vectors from 0 to infinity to be equally weighted. However, there are only k-vectors from 0 to the Fermi wave vector available. The system thus cannot form a localized screening of the impurity spin, but does the closest alternative possibility, which results in an oscillatory spin density surrounding the impurity spin. A second Mn magnetic moment will interact with this oscillatory spin density, and hence will couple ferromagnetically or antiferromagnetically, depending on the sign of the
spin density at that point. The oscillatory character of the RKKY coupling can be neglected as long as the average distance between carriers \( r_c = (4\pi p/3)^{-1/3} \) is much larger than that between the magnetic impurities \( r_s = (4\pi x N_0/3)^{-1/3} \).

The RKKY function changes sign the first time at \( r = 1.17 r_c \). Interestingly the ferromagnetism does not break down at Mn concentrations below the metal to insulator transition as one would expect from RKKY theory. To explain the origin of ferromagnetism in this regime a magnetic polaron model has been proposed [3].

In the Zener model and the RKKY scheme the \( pd \)-hybridization is usually assumed to be spherically isotropic [2]. Only recently Mahadevan et al. predicted a strongly anisotropic \( pd \)-hybridization in Ga\(_{1-x}\)Mn\(_x\)As, taking into account the symmetry of the Mn 3\( d \) levels hybridizing with the As \( p \) orbitals [71]. By the tetrahedral crystal field the Mn 3\( d \) levels are split into \( e_g \) levels with lower energy and \( t_{2g} \) levels with higher energy, respectively. Fully occupied \( t_{2g} \) and \( e_g \) states inside the valence band have mainly Mn \( d \) character whereas the partially filled \( t_{2g} \) states at the valence band are formed of Mn 3\( d \) and As \( p \) orbitals [71]. Assuming spin conserving hopping interactions between those partially occupied levels the exchange interaction between Mn pairs at various distances along different lattice orientations has been studied by total energy ab initio calculations [71]. The main result of these calculations is a significant orientation dependence of the \( pd \)-hybridization and therefore of the exchange coupling [71]. The exchange coupling of Mn pairs oriented along the \( <110> \) axis remains higher in strength compared to that of Mn pairs oriented along other directions even if their separation is smaller [71].

### 3.2.3 Magnetic polarons

Contrary to the Zener model that assumes itinerant carriers (holes) in Ga\(_{1-x}\)Mn\(_x\)As, the idea of magnetic polarons is based on localized holes [74]. Such scenario applies to Ga\(_{1-x}\)Mn\(_x\)As samples with Mn concentrations that are below the metal to insulator transition. The hole wave function is assumed to fall off exponentially from the localization center with the decay length \( a_B \) [74]. Within the localization radius of the hole \( (a_B \approx 1nm \text{ in Ga}_{1-x}\text{Mn}_x\text{As}) \) exchange interaction with the Mn impurities lead to the formation of a bound magnetic polaron [74]. At low enough temperatures neighboring polarons begin to overlap and interact with each other. When the cluster of correlated polarons reaches the percolation limit the ferromagnetic transition occurs. A schematic picture of two magnetic polarons is given in Fig. 3.1. The exponential decay of the two hole wave functions defines a lens shaped region in between the two polarons which is important for the ferromagnetic coupling of the two polarons (indicated by the hatched area in Fig. 3.1). The polaron model predicts the existence of magnetic clusters (magnetic polarons) above the Curie temperature.
3.2 Magnetic ordering in dilute magnetic semiconductors

3.2.4 Double exchange

Also the double exchange mechanism between Mn ions of different valency has been considered as an origin of ferromagnetism. Double exchange is a mechanism for spin coupling between magnetic ions of different valency that arises from electron delocalization. The term double exchange was introduced by Zener to explain the magneto-conductive properties of mixed-valence solid, notably doped Mn perovskites. The ferromagnetic alignment of Mn spins due to double exchange is demonstrated in Fig. 3.2. If the spin down electron of the right Mn atom is allowed to delocalize to the left Mn the hopping can only occur into an orbital that contains a spin up electron (Pauli principle). Since the hopping does not involve spin flips (because the interaction leading to delocalization is spin-independent), the hopping of the electron forces the spins of both metal sites into parallel alignment, resulting in nine unpaired spins.

The difficulties to describe the ferromagnetic ordering in Ga$_{1-x}$Mn$_x$As by an exact model are partially due to the high degree of disorder in this system. The distribution of substitutional Mn, the carrier density and the carrier mobility are strongly influenced by the presence of defects like interstitial Mn or As antisites. Both of them act as double donors [4] and the experimentally observed carrier densities well below the Mn concentration have been assigned to their presence [34]. Furthermore it was proposed that the interstitial Mn tends to align antiferromagnetically with substitutional Mn effectively canceling their moments [10]. Such reduction of the average magnetic moment per Mn atom was observed experimentally [22, 18, 11] but the origin is not clear. It could arise from antiferromagnetic coupling between interstitial and substitutional Mn but it could be also due to antiferromagnetic coupling between substitutional Mn-Mn nearest neighbors. Also magnetic frustration as predicted by [41] could cause such a reduction of the observed magnetic moment. This would explain why this effect
Figure 3.2: Ferromagnetic coupling between Mn$^{2+}$ and Mn$^{1+}$ due to double exchange. Hopping of the spin down electron is only possible for parallel alignment of the localized Mn spins.

was found to remain at Mn concentrations of x=0.06 [22] even if compensating defects such as interstitial Mn donors are removed by post-growth annealing techniques [78].

### 3.3 Magnetic anisotropy

Ferromagnetic materials exhibit intrinsic easy and hard directions of magnetization. This magnetic anisotropy is from a technological and from a fundamental point of view one of the most important properties of magnetic materials. Different applications require different anisotropy. For instance magnetic data storage requires a large magnetic anisotropy barrier between opposite magnetization directions to prevent the loss of information due to thermal magnetic fluctuations. However in magnetic sensors a weak magnetic anisotropy is advantageous so that the magnetization direction can follow external magnetic fields easily. But not only the strength also the symmetry properties of the magnetic anisotropy are of major interest to align the magnetization axis along a preferred direction. In that respect Ga$_{1-x}$Mn$_x$As is a very interesting material since it allows tailoring of the anisotropy by the epitaxial strain, temperature and hole concentration [43, 54]. Depending on these parameters configurations with an out-of-plane or a cubic in-plane magnetic anisotropy have been predicted and experimentally observed [43, 54]. Recently also the combination of a cubic in-plane magnetic anisotropy superposed by an additional uniaxial in-plane magnetic anisotropy has been observed [84]. The complexity of magnetic anisotropy in Ga$_{1-x}$Mn$_x$As indicates already its microscopic origin since the magnetic shape anisotropy term would cause an isotropic in-plane easy axis for lateraly extended thin film samples. Usually
a strong magneto-crystalline anisotropy originating in the electronic structure is characterized by a directional dependence of the orbital magnetic moment. This has been predicted by Bruno [56] and experimentally verified by different groups [66, 67]. The difference of the orbital moments along easy and hard magnetization axis is directly proportional to the magneto-crystalline anisotropy energy [66, 67]. However for Ga$_{1-x}$Mn$_x$As the situation is more complex. The long range ferromagnetic coupling of the Mn impurity 3$d$ spins is mediated by valence holes with a non-zero spin polarization. Strain effects due to a lattice mismatch between the Ga$_{1-x}$Mn$_x$As and the substrate can cause a large valence hole spin anisotropy due to the strong spin-orbit coupling in the GaAs valence band. Thus the out-of-plane or cubic in-plane magnetic anisotropy of Ga$_{1-x}$Mn$_x$As films is explained by the presence of uniaxial tensile or biaxial compressive strain, respectively [54, 84]. E.g. under tensile uniaxial strain the valence band splits into heavy-hole $m_j = \pm 3/2$ and light hole $m_j = \pm 1/2$ subbands. Following a simplified model described in ref. [54] the heavy or light hole character of the carriers depending on the occupation of the two subbands determines the in- or out-of-plane orientation of sample magnetization at remanence. The exchange coupling of valence holes and the Mn 3$d$ impurity spins via the pd-hybridization transfers these complexity into the Mn 3$d$ subsystem.

It is obvious that in Ga$_{1-x}$Mn$_x$As a detailed understanding the Mn 3$d$ configuration is the crucial part to separate the influence of different Mn configurations on the magnetic coupling. This information is not available to standard techniques like SQUID or anomalous Hall current measurements that are commonly used to characterize the magnetic properties. These methods can even not distinguish between contributions from holes or Mn atoms to the magnetization. Soft x-ray spectroscopy is an ideal tool to investigate the electronic and magnetic configuration of the Mn 3$d$ shell. The following chapters will demonstrate that this method is sensitive enough to separate the different Mn species occurring in Ga$_{1-x}$Mn$_x$As and investigate their influence on the ferromagnetic coupling.
Ferromagnetism in dilute magnetic semiconductors
Chapter 4

Experimental considerations

4.1 Sample preparation

The challenge of growing Ga$_{1-x}$Mn$_x$As by molecular beam epitaxy (MBE) is to overcome the limited solubility of Mn in GaAs. At the usual growth temperatures of GaAs (600K), the coevaporation of Mn would lead to the formation of a second phase with MnAs clusters [1]. The formation of MnAs can only be avoided at lower growth temperatures (180 - 300K) in the so called low-temperature MBE. Whereby the actual growth temperature varies with the Mn concentration [1].

The samples presented here were grown at the university of Würzburg at the institute of Prof. L.W. Molenkamp [9] using a GaAs (001) surface as substrate with 80nm low-temperature GaAs layer deposited as a buffer prior to the growth of the Ga$_{1-x}$Mn$_x$As layer. The Mn concentration $x$ for each sample has been determined from the lattice constant as described in ref. [9]. In the present work samples with Mn concentrations ranging from $x=0.007$ to $x=0.062$ that have been investigated as listed in table 4.1. Most of the Ga$_{1-x}$Mn$_x$As films are rather thick compared to literature. Samples that reach a $T_c$ above 140K after annealing usually have a thickness of 50nm or less. This is ascribed to the diffusion of defects like interstitial Mn to the surface during the annealing which is less efficient in thicker samples [15]. Results from ref. [80] indicate that also in the as grown state thinner samples can reach a higher $T_c$. For the x-ray spectroscopy and especially the fluorescence measurements a thicker Ga$_{1-x}$Mn$_x$As layer ensures that the bulk properties can be probed with not too much disturbance from the surface layer.

The surface of the Ga$_{1-x}$Mn$_x$As layer was characterized in situ by RHEED measurements showing a nice epitactic growth and a (2 x 1) surface reconstruction [9]. In addition the roughness of the surface has been analyzed ex-situ by atomic force microscopy (AFM). This topographic information is a valuable input for the evaluation of reflectivity spectra as explained at the end of this chapter. A typical AFM image of the $x=0.017$ sample is shown in Fig. 4.1. On a length scale of several 100nm the surface shows a sinusoidal corrugation with an amplitude...
Experimental considerations

of 6 ± 2nm. Very similar corrugations were present in all other samples except the x=0.062 sample which had a flatter surface. This corrugation is most likely caused by thickness variations of the low-temperature GaAs buffer layer [70]. In addition to the buffer layer corrugation all samples have a rms surface roughness of 0.6 ± 0.2nm that we assign to thickness variations of the Ga$_{1-x}$Mn$_x$As layer.

<table>
<thead>
<tr>
<th>Mn concentration x:</th>
<th>0.008</th>
<th>0.017</th>
<th>0.051</th>
<th>0.062</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curie temperature T$_c$:</td>
<td>12K</td>
<td>25K</td>
<td>55K</td>
<td>65K</td>
</tr>
<tr>
<td>thickness:</td>
<td>350nm</td>
<td>300nm</td>
<td>500nm</td>
<td>180nm</td>
</tr>
</tbody>
</table>

4.1.1 Annealing

A disadvantage of the low-temperature growth is the large number of defects that are introduced. In literature mainly interstitial Mn and As antisites are discussed, because both defects act as double donors and compensate the effect of the Mn acceptors [4]. To remove such defects the samples have to undergo a post growth annealing procedure [15]. The optimum annealing temperature is below the activation threshold of substitutional Mn diffusion but above that of interstitial Mn ($\approx 180^\circ C$). Most of the annealing experiments in the literature have been performed ex situ in air [15]. It has been demonstrated that by low-temperature annealing the carrier concentration and thus T$_c$ can be raised [15]. It is generally agreed that this is due to the removal of interstitial Mn by diffusion. The record values of T$_c$, so far, were obtained by the annealing of samples thinner than 50nm. It is still an open question whether the annealing of thicker samples is inefficient because of the limited diffusion length, or whether the formation of a layer of interstitial Mn at the surface, passivated by oxidation prevents the out-diffusion of the remaining interstitial Mn. The interest of x-ray spectroscopy is to distinguish interstitial Mn from substitutional Mn by its different ground state hybridization. To keep the influence of surface oxidation as small as possible the x = 0.062 sample was annealed at 185$^\circ C$ for 24h in vacuum.

4.2 Experimental setup

The experiments described here were performed at the BESSY UE46 Hahn-Meitner-Institute beamline and at the high field magnet at ID8 at the ESRF. A schematic view of the experimental setup inside the ultra high vacuum chamber at BESSY is given in Fig. 4.2. The sample was mounted on a He cryostat that allowed for temperatures between 10 and 300K. At BESSY the sample holder was equipped with small permanent magnet applying a field of 100- 200 Oe along the horizontal inplane direction of the sample to align the magnetization by field cooling. The fluorescence diode was mounted inside the cold shield collecting the fluorescence photons at an fixed angle of 30$^\circ$ from above with respect to the sample surface. Scattered x-rays were detected by a diode mounted on a scattering
4.2 Experimental setup

Figure 4.1: Atomic force microscopy (AFM) image of the x=0.017 sample. On a length scale of several 100nm we find sinusoidal surface corrugations with an amplitude of 6nm ± 2nm as shown by the line scan. Besides this long distance corrugation a rms roughness of 0.6 ± 0.2nm is present.
Experimental considerations

4.3 Data recording

Due to the thickness of the samples a direct absorption measurement in transmission geometry was not feasible. Instead we recorded the total electron yield and the fluorescence yield which are related to the decay of photoinduced 2p core holes. The two involved decay channels are radiationless Auger decay and the emission of a fluorescent photon. By the Auger process the core hole is re-occupied by an electron of the d-shell, accompanied by the emission of a second electron of the d-shell that compensates energy and momentum. The fluorescent decay is the reversal of the excitation process, the 2p valence is filled by an electron of the d-shell under the emission of a photon that compensates energy and momentum. Within the limitations discussed below both signals the total electron yield and the total fluorescence yield are proportional to the absorption cross section \( \sigma(E) \). To account for intensity variations in the exciting x-ray beam both signals were normalized to the photocurrent of the refocussing mirror.

4.3.1 Total electron yield

The total electron yield signal represents all electrons that escape from the sample surface. A large fraction of these electrons are not Auger electrons generated in the initial x-ray absorption event, but result from inelastic scattering processes along the trajectories of Auger electrons in the sample. The average energy of these secondary electrons is very low with an energy distribution ranging from zero to several 10 eV. This yield of secondary electrons is proportional to the absorption cross section times the photon energy. Since the spin-orbit splitting of the Mn L\(_{2,3}\) edges is small compared to the energy of the L\(_{2,3}\) thresholds, the approximation by a direct relation between the total electron yield (TEY) and the absorption cross section \( \sigma \) is well justified. As shown by Fig. 4.3 the drain current signal is very surface sensitive due to the limited escape depth of Auger electrons and secondary electrons of typically 1-2nm.

4.3.2 Fluorescence yield

The escape depth of fluorescence photons is in general much larger than that of electrons. As shown in Fig. 4.4 the calculated escape depth for a typical
4.3 Data recording

Figure 4.2: Schematic view of the experimental setup at BESY.

Figure 4.3: Energy dependence of the escape depth for electrons. The energies covered by our experiment are marked by red circles.
Experimental considerations

Ga$_{1-x}$Mn$_x$As sample is around 200nm. This makes the fluorescence yield (FY) detection a bulk sensitive signal, but it can also give rise to self absorption effects. In absence of self absorption effects the current recorded from the fluorescence diode is proportional to the absorption cross section $\sigma(E)$ times the photon energy.

4.3.3 Self absorption effects

If the probing depth (escape depth) of the fluorescence yield (FY) or total electron yield (TEY) is of the same order or larger than the attenuation length of the incident x-rays ($1/\sigma(E)$), the proportionality between the recorded signal and the absorption cross section $\sigma(E)$ is likely to be destroyed by self absorption effects. Therefore especially FY detection suffers often from saturation or self absorption effects. These effects arise from the absorption of exciting photons on their way in the sample and from the absorption of fluorescence photons or Auger electrons on their way out of the sample. These effects depend strongly on the experimental geometry as indicated by Fig. 4.5. At grazing incidence angles the attenuation length normal to the surface decreases according to $1/\sigma_{\text{eff}} = \sin\alpha / \sigma$. In the worst case, e.g. for fluorescence detection normal to the sample surface and grazing incidence of the x-ray beam, all the incoming photons get absorbed in a region within the probing depth of the detector. In that case the signal becomes nearly independent of the absorption cross section and proportional to the intensity of the incoming x-ray beam. For a flat sample of the thickness $d$ we can calculate the expected fluorescence intensity $I^x(E)$. Photons of the energy $E$ enter the sample under an incident angle $\alpha$ and get absorbed causing core hole in the level $X$ according to their energy. If this core hole decays via the emission of a fluorescence photon at the energy $E_F$ and this photon leaves the sample it can be detected at the takeoff angle $\beta$. The partial fluorescence intensity excited by the incoming x-ray intensity at the depth $d$ is proportional to [39]:

$$dI^x_d(E) \propto I_0(E) \exp[-(\frac{\sigma(E)}{\sin\alpha} + \frac{\sigma(E_F)}{\sin\beta}) \cdot d] \frac{\sigma_x}{\sin\alpha} dd$$

We obtain the expected fluorescence signal by an integration over the sample thickness $D$:

$$I^x(E) \propto \int_0^D dI^x_d(E) dd$$

All samples investigated in this work consist of a Ga$_{1-x}$Mn$_x$As layer deposited on a GaAs substrate in this case the integral can be substituted by the sum over two discrete layers:
4.3 Data recording

Figure 4.4: Calculated attenuation length for fluorescence photons emitted from a sample with a manganese concentration of \( x = 0.06 \).

Figure 4.5: This figure illustrates the dependence of saturation effects on the experimental geometry. The x-ray beam enters the sample under the glancing angle \( \alpha \) and the fluorescence photons are detected at an detection angle \( \beta \). Strong self absorption effects are expected for grazing incidence of the x-ray beam and the fluorescence detection under \( \beta = 90^\circ \). In that case the way of the fluorescence photons to the detector is short compared to the penetration length. The other extrem is the normal incidence of the x-ray beam and the fluorescence detector at a grazing angle. In this geometry fluorescence photons from deeper levels that experienced self absorption effects can not reach the detector.
Experimental considerations

\[ I^x(E) \propto I_0(E) \cdot \left[ \frac{\sigma_x(E)}{\sin \alpha} \times \left(1 - e^{-\left(\frac{\sigma_{\text{tot}}(E)}{\sin \alpha} + \frac{\sigma_{\text{sub}}(E)}{\sin \beta}\right) d} \right) \right. \\
\left. + \frac{\sigma_{\text{sub}}(E)}{\sin \alpha} \times \left( e^{-\left(\frac{\sigma_{\text{tot}}(E)}{\sin \alpha} + \frac{\sigma_{\text{sub}}(E)}{\sin \beta}\right) d} \right) \right] \]  

(4.3)

Where \( \sigma_x \) is the absorption coefficient related to the production of a core hole in the investigated level \( X \) of the Mn impurities and \( \sigma_{\text{tot}} \) is the total absorption coefficient of the \( \text{Ga}_{1-x}\text{Mn}_x\text{As} \) layer which is the sum of \( \sigma_X \) and \( \sigma_{\text{other}} \) the latter describe the absorption due to shallower core levels, valence levels and other atomic species. The absorption coefficient of the GaAs substrate enters as \( \sigma_{\text{sub}} \) and \( I_0 \) denotes the intensity of the incoming x-ray light. To identify the presence of any self absorption effects in our FY signal we compared spectra recorded at different experimental geometries (i.e. varying the incidence angle of x-ray beam with fixed geometry between sample and detection diode as shown in Fig. 4.2).

Fig. 4.6 shows two XAS spectra of the x=0.062 sample recorded with the fluorescence diode in a fixed detection geometry (constant acceptance angle), only the incidence angle of the exciting x-ray beam was changed. The spectra are normalized to a constant step edge before and after the \( L_2,3 \) absorption edges. This step in the absorption cross section is caused by transition into continuum states. Comparing the XAS spectrum recorded at an incidence angle of 70° (red triangles) to that obtained at an incidence angle of 10° (black circles) we find a decreased peak intensity. This indicates that the fluorescence signal is no longer proportional to the absorption cross section \( \sigma(E) \) due to the presence of self absorption effects. The dependence of the self absorption effects on the incidence angle of the x-ray beam is demonstrated in the inset of Fig. 4.6. It displays the measured \( L_3 \) peak intensity for various incidence angles of the x-ray beam (solid squares). If we scale the measured fluorescence intensities to absolute absorption cross sections, according to the literature data provided by the Center of X-ray Optics [14], we can use equation 4.3 to calculate the intensity seen by the fluorescence diode in dependence on the absorption cross section of the Mn species, the sample thickness and the experimental geometry [39]. We assumed that \( \sigma_{\text{other}} \) and \( \sigma_{\text{sub}} \) are constant within the probed energy interval (from 620eV to 670eV). Thus the energy dependence of saturation effects is determined by the Mn absorption cross section. The calculated reduction of the \( L_3 \) peak intensity due to self absorption effects indicated by the red line in the inset of Fig. 4.6 agrees well with the measurements.

To correct for the saturation effects we can use an iterative algorithm. In the first step we apply equation 4.3 to the measured absorption cross sections and calculate the ratio of measured and saturation reduced intensities at different detection angles. If the ratio is always one no saturation effects are present, if not
4.3 Data recording

Figure 4.6: This figure displays XAS spectra of the x=0.062 sample recorded in fluorescence at the L\textsubscript{2,3} edge of Mn. The sample was kept at room temperature (non magnetic). The fluorescence detector was fixed in respect to the sample surface, pointing on the sample at an angle of 30° in respect to the sample surface. The spectrum displayed by black open circles was recorded with the x-ray beam at an incidence angle of 10°. Whereas for the spectrum displayed by red triangles the incidence angle of the x-ray beam was changed to 70°. The spectra are normalized to a constant step function to visualize the influence of the self absorption effects on the peak intensities. Using an iterative algorithm the spectrum recorded at 70° incidence angle was corrected for saturation effects. The corrected spectrum is displayed as black line. The inset shows the calculated change of the L\textsubscript{3} peak height due to saturation effects in dependence of the incidence angle of the x-ray beam using equation 4.3. The measured L\textsubscript{3} peak intensities for various incidence angles of the x-ray beam are shown as black squares.
the measured absorption cross sections multiplied by the ratio are used as input for the next iteration. The iterations are stopped if the calculated saturation of the input intensities is identical with the measured absorption intensities. Now each point in the measured spectra is multiplied by an intensity dependent factor determined by the algorithm. To confirm the result of our saturation correction we compared the corrected spectra to those recorded at geometries or sample thicknesses for which no saturation effects have been found. In Fig. 4.6 we find excellent agreement between the spectrum of the x=0.06 sample measured at normal incidence and the calculated correction (solid line) of the spectrum recorded at 70° incidence angle (solid triangle).

4.4 Resonant reflectivity

In order to obtain structural information on the Mn distribution in our samples we recorded x-ray resonant reflectivity spectra at the Mn 2\(p \rightarrow 3d\) resonance. The reflectivity is given by:

\[
I \propto |\sum_i f_i \times \exp(iq\mathbf{r}_i)|^2
\]  

(4.4)

where \(f_i\) is the complex scattering amplitude of the atom \(i\) at the position \(\mathbf{r}_i\) and \(q\) the scattering vector. To calculate the reflected intensity we need to know the complex scattering amplitude of the Mn atoms present in our sample. The imaginary part \(\text{Im}(f)\), which describes the attenuation, corresponds to the measured absorption signal. The real part, \(\text{Re}(f)\), can be obtained by a Kramers-Kronig transformation of \(\text{Im}(f)\) as explained in the paragraph below. The different line shape of \(\text{Re}(f)\) and \(\text{Im}(f)\), shown in Fig. 4.7, implies a phase shift between incident and scattered x-rays. This phase shift depends on the chemical composition of the individual layers and leads to interferences as a function of \(q\), i.e. the incidence angle and the photon energy. Since we detect only the intensity and not the phase of the reflected x-rays the measured reflectivity spectra contain not all the information that is needed to determine the chemical depth profile. To extract information from the measured spectra we need to compare them to spectra calculated from a model system. This requires an additional assumption on the structure e.g. the existence of an surface layer, interface roughness, etc.

The calculations were done employing the IMD code [7] which is based on a modified Fresnel coefficient formalism, that takes interface imperfections into account [8]. The Fresnel equations describe the amplitude of the reflected \((E_i)\) and transmitted \((E_j)\) electric fields of a plane electromagnetic wave at an ideal interface of two semi-infinite media with the complex indices of refraction \(n_i\) and \(n_j\). For an incidence angle \(\theta_i\) they read:

\[
\frac{|E_i|}{|E_i|} = \frac{n_i \cos \theta_i - n_j \cos \theta_j}{n_i \cos \theta_i + n_j \cos \theta_j} = r_{ij} 
\]  

(4.5)
4.4 Resonant reflectivity

\[ \frac{|E_j|}{|E_i|} = \frac{2n_i \cos \theta_i}{n_i \cos \theta_i + n_j \cos \theta_j} = t_{ij} \]  \hspace{1cm} (4.6)

Where \( \theta_j \) is the angle of refraction and \( r_{ij} \) and \( t_{ij} \) are the Fresnel reflection and transmission coefficients, respectively. Interface imperfections like roughness or diffuseness are included in the Fresnel equations following a formalism developed by Stearns [8]. In this formalism the interface is described by a profile function \( p(z) \) (\( z \) along the surface normal). The profile function is defined as the normalized average value of the dielectric function \( \epsilon(x) \) (with \( n = \sqrt{\epsilon} \)) along the \( z \)-direction.

\[ P(z) = \frac{\int \int \epsilon(x)dx dy}{(\epsilon_i - \epsilon_f) \int \int dx dy} \]  \hspace{1cm} (4.7)

As demonstrated in ref. [8] the loss in specular reflectivity resulting from interface imperfections can be approximated by multiplying the Fresnel coefficients with the Fourier transform of the function \( w_z = dp/dz \). The new Fresnel coefficients are now:

\[ r'_{ij} = r_{ij} \tilde{w}(s_i), \]  \hspace{1cm} (4.8)

with \( s_i = 4\pi \theta_i/\lambda \) and \( \lambda \) the wavelength of the light. Four different profile functions have been developed in ref. [8], describing the interface profile by a error function, exponential function, linear function or sinusoidal function. The explicit terms are given in ref. [8]. The width of the interface is described by the parameter \( \sigma \), for a purely rough interface \( \sigma \) corresponds to the rms roughness.

In the case of a multilayer system consisting of \( N \) layers and \( N+1 \) interfaces in which the \( i \)-th layer has the thickness \( d_i \) the roughness \( \sigma_i \) and the index of refraction \( n_i \), the net reflection and transmission coefficients of the \( i \)-th layer are given by [40]:

\[ r_i = \frac{r_{ij} + r_j e^{2i\beta_i}}{1 + r_{ij} r_j e^{2i\beta_i}}; \quad \text{with} \quad \beta_i = 2\pi d_i n_i / \lambda \]  \hspace{1cm} (4.9)

\[ t_i = \frac{t_{ij} t_j e^{2i\beta_i}}{1 + r_{ij} r_j e^{2i\beta_i}} \]  \hspace{1cm} (4.10)

To compute the net reflection and transmission coefficients of the multilayer the IMD code applies equations 4.9 and 4.10 recursively, starting at the bottom layer.

**Kramers Kronig Transformation**

The imaginary part of the scattering factor \( \text{Im}(f) \) can be determined from the total absorption cross section \( \sigma(\omega) \) that is proportional to the measured total electron yield and fluorescence yield signal. Their relation is given by: \( \text{Im}(f)(\omega) = \omega \sigma(\omega) / 4\pi r_0 \), Where \( r_0 \) is the classical electron radius, \( c \) the speed of light and \( \omega \) the incident x-ray frequency. To obtain the absolute absorption cross section the normalized absorption spectra were multiplied by a scaling factor. We choose a
Figure 4.7: The figure shows the real (panel A) and the imaginary (panel B) part of the optical constants for substitutional Mn (black line) and Mn in a $3d^5$ configuration (red line). The imaginary part was determined by x-ray absorption spectroscopy, the real part was calculated by a Kramers Kronig relation using equation 4.11.
4.4 Resonant reflectivity

scaling factor that forced the measured absorption cross section before and after the $L_{2,3}$ resonances to be identical with the data provided by the Center of X-ray Optics at the Berkley Lab [14]. Then we calculated the real part of the scattering factor $\text{Re}(f)$ from the imaginary part using a Kramers Kronig relation. These dispersion relations couple the real and the imaginary part of the atomic scattering amplitude by a Hilbert transformation:

$$\text{Re}(f)(\omega_0) = 1 + \frac{2}{\pi} P \int_{0}^{\infty} \frac{\omega \text{Im}(f)(\omega)}{\omega_0^2 - \omega^2} d\omega. \quad (4.11)$$

Two obstacles for the practical application of the Kramers-Kronig relations exist. First we need to know the absorption coefficient at all energies to determine the real part. And second a singularity in the Cauchy principal value integral occurs. In our experiment we measure the absorption coefficient only in a short energy range from 620 – 670 eV photon energy covering the $L_{2,3}$ absorption edges of Mn. To calculate the real part of $f$ with the above formula we extended the energy range of the measured data set to several hundred eV. We did this by adding literature data obtained from the Center of X-ray Optics on the low and the high energy side of the measured data set. Values outside the integration limits are replaced by a constant.

The presence of the singularity at $\omega_0$ in the cauchy integral requires that the equation is manipulated to allow numerical integration. The integral can be split into three parts with the singularity in the second part, where $a$ and $b$ denote the adjacent points below and above the singularity.
Experimental considerations

\[
\frac{2P}{\pi} \int_0^\infty \frac{\omega \cdot \text{Im}(f)(\omega)}{\omega_0^2 - \omega^2} = \frac{2}{\pi} \int_0^a \frac{\omega \cdot \text{Im}(f)(\omega)}{\omega_0^2 - \omega^2} + \frac{2}{\pi} \int_a^b \frac{\omega \cdot \text{Im}(f)(\omega)}{\omega_0^2 - \omega^2} + \frac{2}{\pi} \int_b^\infty \frac{\omega \cdot \text{Im}(f)(\omega)}{\omega_0^2 - \omega^2}
\]

(4.12)

The integral containing the singularity can be rewritten as:

\[
\frac{2P}{\pi} \int_a^b \frac{\omega \cdot \text{Im}(f)(\omega)}{\omega_0^2 - \omega^2} = \frac{1}{\pi} \left( -P \int_a^b \frac{\text{Im}(f)(\omega)}{\omega_0 - \omega} - P \int_a^b \text{Im}(f)(\omega) \right)
\]

(4.13)

Hoyt et al. [5] demonstrated that if we expand \(\text{Re}(f)(\omega)\) in a Taylor series about \(\omega_0\) the integral on the interval \(a \to b\) becomes numerically calculable. It reads now [5]:

\[
\frac{2P}{\pi} \int_a^b \frac{\omega \cdot \text{Im}(f)(\omega)}{\omega_0^2 - \omega^2} = \frac{1}{\pi} \left[ P \int_a^b \frac{-\text{Im}(f)(\omega)}{\omega_0 + \omega} d\omega \right.
\]

\[
-\left\{ \ln|b - \omega_0| - \ln|a - \omega_0| \right\} - \left. \frac{d\text{Im}(f)}{d\omega} \right|_{\omega_0}(b - a)
\]

\[
- \sum_{n=2}^{\infty} \frac{1}{(n)n!} \frac{d^n\text{Im}(f)}{d\omega^n} \left|_{\omega_0}(b - \omega_0)^n - (a - \omega_0)^n \right]
\]

(4.14)

By substituting 4.14 into 4.12 we can now use equation 4.11 to calculate the real part of the atomic scattering factor. Results obtained from the Kramers Kronig transformation are shown in Fig. 4.7. In this case we applied the transformation to two different Mn electronic configurations present in our Ga\(_{1-x}\)Mn\(_x\)As samples. The figure displays the index of refraction \(n\) which we used as input for the IMD code. The index of refraction can be calculated from the atomic scattering factor by \((\text{Re}(n) + i\text{Im}(n))(\omega) = 1 - N\rho_0(c/\omega)^2 \cdot (\text{Re}(f) + i\text{Im}(f))(\omega)/2\pi\). Where \(N\) is the number of atoms per unit.
Chapter 5

Chemical and magnetical depth profile of Ga$_{1-x}$Mn$_x$As films

For the understanding of the ferromagnetic ordering the electronic configuration of the Mn impurities and the number of Mn atoms contributing to the long range ferromagnetic order are of major interest. These parameters can be probed directly by x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD). At the Mn $2p$ - $3d$ resonance the XAS and MXCD line shapes are characteristic for the Mn $3d$ electronic and magnetic configuration respectively [51]. Although these techniques have been applied to Ga$_{1-x}$Mn$_x$As previously [11, 18, 13, 16, 21] the results are in some points inconsistent. The first experiments [11, 18] found a pronounced multiplet structure in the Mn XAS spectra characteristic of a highly localized state. The weak XMCD signal indicated that only a fraction of 13% of the Mn atoms participate in the long range ferromagnetic ordering. Changes in the line shape of the Mn XAS spectra before and after annealing have been observed indicating that more than one Mn species must be present in Ga$_{1-x}$Mn$_x$As [13]. More recently XAS spectra with less pronounced multiplet structure have been reported [16] in combination with remarkably high numbers (66%) of ferromagnetically aligned Mn impurities in Ga$_{1-x}$Mn$_x$As [16]. It has been proposed very recently [21] that this discrepancy may be caused by a Mn rich surface layer.

In this chapter we study the chemical depth profile of as-grown and annealed Ga$_{1-x}$Mn$_x$As samples. As-grown refers to MBE grown samples that were transported through air and measured in our UHV setup without surface preparation. The annealing was done in a separate vacuum chamber with a short exposure to air during the transfer into the measurement chamber. The presented XAS and XMCD experiments exploit the different probing depth of flourescence and electron yield detection to resolve bulk and surface properties of the Mn impurities. Comparing bulk and surface sensitive XAS and XMCD spectra two Mn species can be identified. The bulk is dominated by ferromagnetic Mn in a mixed valence $3d^5 - 3d^6$ electronic configuration. This has been assigned to substitutional Mn
hybridizing with the GaAs host [11]. At the surface substitutional Mn and a second non-ferromagnetic Mn species in a localized 3d$^5$ configuration is observed. The contributions of both Mn species to the spectra are clearly discernible by their different multiplet structure and a 0.6eV core level shift of the 2p - 3d resonance. The depth profile of both Mn species in the Ga$_{1-x}$Mn$_x$As films is obtained by x-ray resonant reflectivity measurements. The results show a non-homogenous depth profile of two Mn species which is present in all as-grown samples with various Mn concentrations ranging from $x=0.01$ to 0.062. To explore the origin of this Mn distribution we tested the effect of low temperature annealing on the Mn depth profile. The $x=0.062$ sample was annealed for 24h at 185°C ex-situ in vacuum. A strongly enhanced surface accumulation of the non-ferromagnetic Mn species after low-temperature annealing is observed, indicating that the non-ferromagnetic species at the surface could be due to diffusion of interstitial Mn out of the bulk. Finally the quantified Mn concentrations can be used to evaluate the effect of the two Mn species on the ferromagnetic coupling.

5.1 Experimental results

5.1.1 Surface magnetization deficit

Fig. 5.1 shows XAS and XMCD spectra of the as-grown $x=0.017$ sample recorded with total electron and fluorescence yield detection at the Mn 2p - 3d resonance. The spectra display two pronounced edges due to transitions into localized 3d states producing 2$p_{3/2}$ and 2$p_{1/2}$ core holes. The XAS spectra are normalized to a constant step like background caused by transitions into continuum states. The XAS multiplet structure obtained with bulk sensitive fluorescence yield (open circles) is very different from that seen with surface sensitive total electron yield (solid circles) detection. In addition the 2p-3d resonance maximum in total electron yield is shifted to 0.6eV higher photon energy compared to the fluorescence spectrum. In contrast the XMCD lineshape in remanence is very similar for both detection methods as shown in Fig. 5.1 B. With an applied field of 2.5T the amplitude of the bulk XMCD spectra increases, but the line shape is still identical with the spectrum taken at remanence. In the surface sensitive XMCD spectra a second peak appears with the applied field as shown in Fig. 5.1 C. The second peak is shifted to 0.6eV higher photon energy compared to the XMCD spectrum recorded at remanence and it corresponds to the 2p-3d resonance maximum in total electron yield XAS (see Fig. 5.1 A). The maximum asymmetry, i.e. the ratio of maximum XMCD and XAS intensity, in the fluorescence yield channel is 22 $\pm$ 1.4% in remanence and 49 $\pm$ 1.3% with an applied magnetic field of 2.5T. In the total electron yield we obtain an asymmetry of 5.6 $\pm$ 1.8% in remanence and 14.9 $\pm$ 1.3% with an applied field of 2.5T. This is much less than in the fluorescence yield spectra.
5.1 Experimental results

Figure 5.1: A) Normalized XAS spectra of ($\text{Ga}_{1-x}\text{Mn}_x$)As with $x=0.017$ recorded at x-ray incidence of $\Theta = 23^\circ$ using fluorescence yield (open circles) and total electron yield (solid squares) detection. B) shows the corresponding XMCD spectra in remanence and C) at an external field of 2.5T applied along the photon incidence direction.
XAS and XMCD line shapes at the 2p-3d resonance are characteristic for the 3d valence configuration [51]. The very different XAS line shapes in Fig. 5.1 A, therefore, point to different Mn species in the bulk and at the surface of the Ga$_{1-x}$Mn$_x$As films. The bulk XAS lineshape corresponds to that observed in ref. [21] after removing a surface layer. It was assigned to a single Mn species in a hybridized ground state with 16% 3d$^4$, 58% 3d$^5$ and 26% 3d$^6$ character (see chapter 6). The observed bulk XMCD line shape is identical to that reported previously [11, 16]. It was assigned to a 80% 3d$^5$, 20% 3d$^6$ hybridized Mn ground state [11] in good agreement with the XAS results. In the following the bulk XAS and XMCD line shapes are assigned to one species named Mn$^I$.

The identical XMCD signal at remanence in the bulk and at the surface demonstrates that Mn$^I$ contributes to the surface signal, too. Therefore the surface signal must result from more than one Mn species since the XAS spectrum is obviously dominated by a different Mn species. Further evidence is provided by the XAS line shape changes that are observed upon annealing as shown in Fig. 5.2. Typical spectra of the x=0.062 sample are shown before (lines) and after (symbols) annealing. In the total electron yield we find a reduced intensity for the low photon energy shoulder of the XAS spectrum after annealing (see Fig. 5.2 A). This shoulder corresponds to the main XAS peak observed in the bulk sensitive fluorescence yield data (see Fig. 5.2B). Similar changes are also visible in the total electron yield XMCD spectra recorded with an applied field of 2.5T (see Fig. 5.2 C). The shoulder corresponding to the bulk XMCD spectrum is reduced in intensity by annealing. In addition the maximum XMCD asymmetry is reduced by a factor of 3.1 as shown in Fig. 5.2 C. In the fluorescence yield spectra an additional multiplet structure appears in the XAS spectra of the annealed sample (see open circles in Fig. 5.2 B). This structure is identical to the one observed with electron yield. It is absent in the spectra after removing the surface layer by Ar-ion sputtering as shown by the crosses in Fig. 5.2 B. Interestingly the additional multiplet structures do not contribute to the XMCD signal in the fluorescence yield, i.e. they correspond to non-ferromagnetically ordered Mn. The XMCD spectra recorded in fluorescence yield before and after annealing have almost identical line shapes. The XMCD asymmetry in the fluorescence yield is reduced by about 14% in the annealed spectrum. This means that annealing enhances the surface segregation of a second Mn species that is paramagnetic at the surface, which is probed by the total electron yield, but in buried layers, that are probe by the fluorescence yield, the second Mn species has either no magnetic moment or is antiferromagentically coupled.

The measured total electron yield XAS spectrum of Fig. 5.1 A) can be decomposed if we assume that the low photon energy shoulder at a photon energy of 640eV visible in Fig. 5.2 A is caused by the Mn$^I$ contribution. Such an assignment is strengthened by the observed annealing dependence of the spectral line shape. Following this idea also the total electron yield XMCD spectrum recorded at 2.5 T external magnetic field can be decomposed into contributions of two different
5.1 Experimental results

Figure 5.2: A) Total electron yield XAS and B) fluorescence yield XAS spectra of the as-grown (solid line) and annealed (symbols) $x=0.062$ sample. C) The corresponding XMCD spectra for both signals, recorded at 2.5T external magnetic field.
Figure 5.3: Spectra of the $x=0.017$ sample are displayed. A) shows the decomposition of the electron yield XAS spectrum (solid line) into the bulk species Mn$_I$ (open circles) and the remaining Mn$_{II}$ (crosses) contributions as described in the text. The decomposition of the corresponding XMCD spectrum recorded at 2.5T is demonstrated in B). A comparison between the Mn$_{II}$ (crosses) line shape and calculated Mn 3$d^5$ XAS and XMCD spectra [51, 6] (black lines) is displayed in the inset of panel A). The magnetization curves for the two species are shown in the inset of panel B).
Mn species, since only in the surface sensitive spectrum an external magnetic field causes a dramatic change in the line shape. This decomposition was done according to that of the XAS spectrum by assuming that the low photon energy shoulder in the XMCD signal recorded at 2.5T corresponds to the bulk XMCD peak of Mn$_I$ atoms (see Fig. 5.2 C). The results of this analysis are displayed in Figs. 5.3 A and B. The remaining surface XAS and XMCD lineshapes agree with multiplet calculations for a 3$d^5$ configuration [51] as shown in the inset of Fig. 5.3 A. No other decomposition gives a similar agreement. This Mn 3$d^5$ species is denoted as Mn$_{II}$ in the following. The magnetization curves versus applied magnetic field for the two Mn species are shown in the inset of Fig. 5.3 B. For the Mn$_I$ species we find a mixture of ferromagnetic and paramagnetic moments. The ferromagnetic coupling increases at higher Mn concentrations (magnetization curves for different Mn concentrations are shown in the next chapter in Fig. 6.5). Atoms of the Mn$_{II}$ species have an uncompensated magnetic moment only at the surface (probed only by total electron yield) which is paramagnetic in all samples.

5.1.2 Chemical depth profile probed by resonant x-ray reflectivity

So far the XAS spectra demonstrated the existence of two Mn species. Mn$_{II}$ obviously accumulates at the surface and can be distinguished from the bulk Mn$_I$ species by XAS. The aim is now to obtain more detailed information on the depth profile of the two Mn species. This was done by using x-ray resonant reflectivity at the Mn 2$d$ – 3$d$ resonance. Reflectivity spectra for the $x = 0.017$ sample are displayed in Fig. 5.4 A. The spectral line shape differs from the XAS spectra measured by fluorescence and total electron yield since the reflected intensity is modulated by interference between incident and reflected photons. As indicated by equation 4.4 the scattering phase shifts and the resulting interference are determined by the spatial Mn distribution and the scattering vector i.e. the photon energy and the incidence angle. The dependence on the latter is demonstrated in Fig. 5.4 A. With decreasing incidence angle we observe a decreasing resonance peak height and the development of a dip on its low energy side. The sensitivity to changes in the Mn distribution is obvious if we compare the signal of the as-grown and the annealed $x = 0.062$ sample in Fig. 5.4 B. At identical incidence angle we find a change in the reflectivity spectrum caused by a rearrangement of interstitial Mn during annealing.

As mentioned in chapter 4 the reflectivity spectra cannot be transformed directly into a distribution of Mn atoms, since only the reflected intensity is recorded while the phase information is lost. For the evaluation a fitting algorithm is used, comparing the measured reflectivity spectra to those calculated from a model structure, using the Mn distribution as a fit parameter. Because
Figure 5.4: A) X-ray resonant reflectivity spectra of the $x=0.0175$ sample (open circles) recorded at incidence angles of $\alpha=27^\circ$, $\beta=23^\circ$, $\gamma=19^\circ$). For clarity a vertical offset has been applied to the spectra. The fits to the spectra are shown as black lines. B) Reflectivity spectra of the $x=0.062$ sample before (open triangles) and after (solid squares) annealing. The fits to the spectra are shown as black lines. The inset shows the enlarged the pre edge part of the spectra.
5.1 Experimental results

the specular reflectivity is sensitive only to the vertical Mn distribution, it is reasonable to model the reflectivity data by a system of different layers that are assumed to be homogenous in the lateral directions. The model describes the sample by three layers, the simplest configuration that is in agreement with the absorption measurements. As shown in the inset of Fig. 5.6 A) the three layers are: (i) the low-temperature GaAs substrate with semi-infinite thickness, (ii) the bulk Ga$_{1-x}$Mn$_x$As layer with given thickness and Mn$_I$ concentration (x) and (iii) a surface layer with variable thickness and concentrations of Mn$_{II}$ and Mn$_I$. Predetermined input parameters of the model are the bulk Mn$_I$ concentration, the thickness of the Ga$_{1-x}$Mn$_x$As layer, the interface roughness, and the index of refraction for both Mn species and the GaAs substrate. The rms roughness for the investigated samples was determined by atomic force microscopy as shown in Fig. 4.1. The index of refraction for two Mn species was determined from the absorption coefficient as explained in chapter 4. The explicit energy dependence of the indices of refraction for Mn$_I$ and Mn$_{II}$ used in the calculations are shown in Fig. 4.7. The index of refraction of the GaAs substrate was taken from literature [14].

Within the model two scenarios are possible. The simplest case would be that the surface layer is formed only by Mn$_{II}$ atoms. But if Mn$_I$ is excluded from the surface layer the resulting fit is of very poor quality indicating that this model is incorrect. The measured reflectivity spectra can only be fitted if we assume that Mn$_{II}$ and Mn$_I$ coexist in the surface layer. In this case we find a perfect agreement between the measured spectra and the fit at all measured angles and photon energies as demonstrated in Fig. 5.4 B. An example how sensitive the calculated reflectivity spectrum depends on the the Mn$_I$ concentration in the surface layer is given by Fig. 5.5. It shows the measured reflectivity spectrum of the x=0.62 sample recorded at an incidence angle of $\theta = 22^\circ$ (open circles). By the fit the Mn$_I$ surface concentration was determined to be x=0.09 (solid line). Keeping the Mn$_I$ concentration fixed at a value of 20% away from the optimum causes a rather large error in the fit, as visible by the line shapes obtained with the Mn$_I$ concentration fixed at x=0.11 (dashed line) or x=0.07 (dotted line). Such tests were preformed for each of the three fit parameters to estimate the error of this method.

The thickness of the surface layer and the Mn concentrations, that were determined by the fit, are summarized for all samples in Fig. 5.6. All as-grown samples have a surface layer of similar thickness (1.5 - 2nm). The Mn$_I$ concentration in the surface layer (solid circles in Fig. 5B) is found to be slightly higher than in the bulk. As expected from the XAS data we find additionally a high concentration of Mn$_{II}$ atoms in the surface layer, which is well above the bulk concentration of Mn$_I$ atoms in all samples. As mentioned above Mn$_I$ and Mn$_{II}$ coexist in the surface layer which means that the total density of Mn in the sur-
Figure 5.5: The confidence interval for the Mn concentrations determined from the fit to the reflectivity spectra (shown is the reflectivity spectrum of the \(x=0.62\) sample recorded at \(\theta = 22^\circ\)). By the best fit the Mn surface concentration was found to be \(x=0.09\). Significantly worse results are obtained if the Mn surface concentration is fixed at \(x=0.11\) (dashed line) or \(x=0.07\) (dotted line).
Figure 5.6: Summary of results for all samples shown as a function of Mn concentration. Solid symbols refer to the as-grown, open symbols to the annealed samples. A) displays the thickness of the surface layer. B) shows the concentrations of Mn$_I$ (circles) and Mn$_{II}$ (square) in the surface layer derived from fits to the reflectivity signal. The lower two panel show the Mn$_I$ XMCD asymmetry in the bulk (triangles) and at the surface (diamonds) normalized to the Mn$_I$ concentration. The values in C) are obtained in remanence and in D) at 2.5T external magnetic field applied along the in-plane direction.
face layer is more than two times above the bulk value. After annealing we find the Mn_{II} concentration in the surface layer strongly enhanced accompanied by an increase in thickness of the surface layer from below 2nm to around 6nm (see Fig. 5.6). Obviously the total amount of Mn_{II} at the surface has strongly increased, whereas the Mn_{I} distribution is hardly affected by the annealing process.

It is important to note that the measured and calculated reflectivity spectra are influenced by interface roughness. This is demonstrated by the reflectivity spectra of the x = 0.062 sample, recorded before and after annealing, which are displayed in the inset of Fig. 5.5 B. In the as-grown state (open triangles) relatively smooth interfaces lead to interference fringes caused by the finite thickness of the Ga_{1-x}Mn_{x}As layer. This is visible as intensity oscillations in the inset of Fig. 5.5 B. The oscillations can be fitted for an interface roughness of 0.65 \pm 0.1nm and a bulk layer thickness of 171 \pm 8nm. These values are in perfect agreement with the surface roughness of 0.6 \pm 0.2nm obtained by atomic force microscopy and the Ga_{1-x}Mn_{x}As layer thickness known from the growth parameters, respectively. After annealing these oscillations disappear (solid squares). This can only be reproduced by our model if we assume an interface region between Ga_{1-x}Mn_{x} and the LT GaAs layer with a gradual change of the Mn concentration. To suppress the oscillations completely, as observed in the experiment, the width of this region has to be 3nm or more. This indicates that diffusion of interstitial Mn during the low temperature annealing does not only take place towards the surface but also into the substrate.

5.2 Discussion

The experimental results presented in this chapter are summarized in Fig. 5.6. Panels A and B contain results from the reflectivity measurements while panels C and D summarize the XMCD results. Although the Ga_{1-x}Mn_{x}As layer thickness differs from sample to sample, the thickness of the surface layer of 1.5 - 2nm is quite uniform for all as-grown samples (see Fig. 5.6 A). After annealing the surface layer thickness increases strongly. All samples exhibit a coexistence of Mn_{I} and Mn_{II} in the surface layer. The total Mn concentration in the surface is more than two times higher than that in the bulk. Even the Mn_{II} concentration itself (solid squares in Fig. 5.6 B) is higher than the bulk Mn_{I} concentration for all samples (dotted line in Fig. 5.6 B). Low-temperature annealing leads to a strong enhancement of the Mn_{II} surface concentration (see Fig. 5.6 B). No significant changes in the Mn_{I} surface concentration are observed (open circle in Fig. 5.6 B). The ratio of Mn_{I} and Mn_{II} in the surface layer obtained from the reflectivity data (Fig. 5.6 B) agrees with that obtained from decomposition of the electron yield XAS spectra. Also the changes upon annealing are reflected in the total electron and fluorescence yield XAS spectra displayed in the Fig. 5.2 A and B, respectively. The change in the ratio between Mn_{I} and Mn_{II}
at the surface reduces the weight of the Mn$_I$ peak in the surface signal. The shoulder corresponding to the Mn$_I$ 2$p$-3$d$ resonance peak (marked by the arrow in Fig. 5.2 A) is less pronounced in the annealed electron yield spectrum. The fluorescence yield signal averages over a large probing depth compared to the total electron yield. In the as-grown sample the surface layer is obviously only a minor contribution to the fluorescence signal and below the detection limit. After annealing the Mn$_{II}$ surface concentration is enhanced by six times and becomes visible in the annealed fluorescence yield XAS spectrum (open circles) as a second peak that corresponds to the Mn$_{II}$ 2$p$-3$d$ resonance peak.

The XMCD results for Mn$_I$ are summarized in Figs. 5.6 C and D. The bulk XMCD asymmetries (triangles) were directly taken from the fluorescence yield data. The surface XMCD values (diamonds) correspond to the measured total electron yield XMCD asymmetries normalized to the fraction of surface Mn$_I$. In remanence we observe a decline of the bulk magnetization (solid triangles in Fig. 5.6 C) with lower Mn concentration. This is most likely due to the reduction of the magnetic ordering temperature. At an external magnetic field of 2.5T the low concentration samples exhibit the highest asymmetry of $0.49 \pm 0.013$ as shown in Fig. 5.6 D. Using the calculated XMCD asymmetries in ref. [11] this would correspond to $83 \pm 4\%$ of the Mn atoms that are magnetically ordered if every Mn atom carries a magnetic moment of $4.6\mu_B$. Interestingly the bulk saturation magnetization of the x=0.062 sample in the as-grown state is smaller than this value of the low concentration sample. Annealing causes a somewhat lower bulk magnetic moment (open triangle) even though it raises the Curie temperature of this sample by 13K. A lower magnetic moment per Mn atom in high concentration samples and its reduction upon annealing has also been observed in ref. [22]. The origin of this effect is discussed in detail in chapter 6. In remanence and with an external magnetic field we find a clearly reduced magnetic moment of surface Mn$_I$ (solid diamonds in Fig. 5.6 C and D) which is further reduced after annealing (open diamond). The ferromagnetic exchange coupling of Mn$_I$ atoms is obviously weaker in the presence of Mn$_{II}$. Possible mechanisms that could cause this effect are discussed below.

The XAS data of Fig. 2 and the resonant reflectivity data summarized in Fig. 5.6 B show an inhomogeneous distribution of two Mn species. From its ferromagnetic and electronic configuration Mn$_I$ can be clearly identified as substitutional Mn replacing the Ga atoms. Mn$_I$ is the dominant species in the bulk of all films. The consistently higher surface concentration of substitutional Mn points to a non-equilibrium MBE growth process as the reason for disorder. Possible site exchanges are then energetically more favorable [20]. Post growth annealing produces hardly any change in the Mn$_I$ surface species (open and solid circles in of Fig. 5.6 B).

It is tempting to assign the second observed Mn species, Mn$_{II}$, characterized by a 3$d^5$ electronic configuration to interstitial Mn. The growth process is known to provide pathways for the generation of interstitial Mn [20], i.e. the
concentration of interstitial Mn at the surface should be significantly higher. In addition the diffusion of interstitial Mn from bulk to the surface during annealing has been observed [15]. This is consistent with the increased accumulation of Mn$_{II}$ at the surface of the $x=0.062$ sample after annealing. Assuming that the accumulation of Mn$_{II}$ at the surface is due to diffusion of interstitials out of the bulk one can estimate that $5 \pm 1\%$ of interstitial Mn was present in the bulk of the as-grown sample. Such an amount of interstitial Mn is less than the value of $17\%$ recently obtained from ion channeling in the bulk of a Ga$_{1-x}$Mn$_x$As sample [19]. However, the number of interstitial Mn in the bulk may strongly depend on the growth conditions. On the other hand the reflectivity data indicate that Mn diffuses not only to the surface but also into the substrate. The accumulation of Mn$_{II}$ in the surface layer is accompanied by magnetization deficit of the Mn$_I$ residing in that layer. It has been proposed that interstitial Mn should couple antiferromagnetically with substitutional Mn and hybridize less with the substrate [10]. The latter seems to be reflected in the $3d^5$ configuration of Mn$_{II}$ which is more localized than that of substitutional Mn ($\text{Mn}_{II}$). But the XMCD spectra provide only little evidence of antiferromagnetic coupling between Mn$_{II}$ and substitutional Mn. Only a small change in the XMCD lineshape that is present in the as-grown $x=0.062$ sample and dissappears after the annealing is visible in Fig. 6.3. It is more likely that the double exchange between substitutional Mn is influenced via interstitial Mn acting as electron donor. This could lead to a reduced carrier concentration in the surface layer, thus reducing $T_c$.

The presence of Mn$_{II}$ at the surface and its enhancement upon annealing is clearly due to the diffusion of interstitial Mn, but the observed lineshape can not be unambiguously identified as interstitial Mn since one can not rule out the influence of surface oxidation as reported previously [15]. In some publication it is argued that the complete out diffusion of interstitial Mn is only possible in the presence of oxygen or nitrogen passivating interstitial Mn at the surface [62]. The annealing of the $x=0.062$ sample was done under vacuum. Following this argument would mean that possibly not all interstitial Mn was removed, because of the limited amount of oxygen that was present at the surface. Interestingly the data indicate that two different magnetic configurations of the Mn$_{II}$ species are present in the surface layer after the annealing. The outer Mn$_{II}$ atoms accessible to the electron yield, which are probaly oxidized, carry a paramagnetic moment. But the buried Mn$_{II}$ atoms visible in the fluorescence yield after annealing have no paramagnetic moment or are strongly antiferromagnetically aligned even at 2.5T external field. This and the coexistence of ferromagnetically ordered Mn$_I$ at the same depth below the surface indicates that the surface layer is not completely oxidized.

Also the Mn bulk spectra could possibly answer the question whether the Mn$_{II}$ configuration is formed at the surface or is also present in the bulk in a very dilute form. If we assume that the Mn$_{II}$ atoms were homogenously distributed in the bulk before the annealing, we can estimate the change of the bulk XAS
lineshape upon their removal. The FY spectrum of the as-grown sample and that of the annealed sample after removing the surface layer by Ar sputtering should show a slight difference due to the missing Mn$^{II}$ in the bulk. These two FY spectra are displayed in Fig. 5.7 (normalized to the same step like background). They are compared to a reference spectrum (open squares) that was generated by subtracting the Mn$^{II}$ lineshape from the as-grown bulk XAS spectrum, according to a spectral weight of 5% Mn$^{II}$. As indicated by the reference signal the removal of 5% Mn$^{II}$ from the bulk should cause a small change in the FY signal at the high energy side of the Mn$^I$ 2p – 3d resonance which is above the detection limit. Interestingly the experimental data show an obvious deviation in the spectral lineshape between the as-grown and the annealed and sputtered sample on the low energy side of the Mn$^I$ 2p – 3d resonance. This effect will be discussed in the next chapter in detail. But the expected change on the high energy side of the Mn$^I$ 2p – 3d resonance is not observed. This points to the influence of surface oxidation. But still, the surface could be altered by sputtering or the Mn$^{II}$ not completely removed.

It is interesting to compare this results to recent neutron scattering experiments [12] which studied depth dependent the magnetic and structural properties of Mn in a x=0.073 sample as-grown and after annealing. The XAS and reflectivity data demonstrate an increased Mn surface concentration in the as-grown samples which is strongly increased upon annealing. By neutron scattering such surface accumulation of Mn could only be found after annealing. In contradic-


tion to the neutron scattering data the XMCD measurements can not confirm a zero magnetic moment of the Mn surface atoms. Their magnetic moment is only reduced compared to the bulk Mn. In addition the bulk magnetic moment measured by XMCD was found to decrease slightly after annealing whereas an increase was seen by neutron scattering. The inconsistent results that both methods obtain for the surface layer may be due to the limited sensitivity of neutron scattering experiments to layers of a few nm. Whether the bulk magnetic moment of Mn is increased or decreased by annealing may also depend on the annealing conditions as time and temperature and the presence of ambient gases. In that respect the annealing conditions were not identical. However, the decrease upon annealing has been also observed by SQUID measurements [22].

5.3 Conclusion

The analysis of the chemical and magnetical depth profile of the Ga$_{1-x}$Mn$_x$As samples revealed the presence of two different Mn species with different XAS and XMCD line shapes in our samples. The bulk of the Ga$_{1-x}$Mn$_x$As samples is dominated by substitutional Mn. This species can easily be identified by its ferromagnetic properties and a mixed valence $3d^5$ - $3d^6$ electronic configuration which is characteristic for the hybridization with GaAs valence orbitals. At the
Figure 5.7: Lineshape analysis of the fluorescence yield spectrum obtained from the x=0.062 sample in the as-grown state (solid line) and after annealing and Ar sputtering (crosses). The reference signal (open squares) was generated by subtracting the Mn$_{II}$ lineshape (dotted line) from the as-grown bulk XAS spectrum according to 5% Mn$_{II}$ in the sample volume.

surface we find an accumulation of non-ferromagnetic Mn in a 3$d^5$ electronic configuration. The enhanced surface segregation of this second Mn species upon annealing of the as-grown samples and the pronounced surface magnetization deficit of substitutional Mn provides strong evidence that the second Mn species is related to interstitial Mn. We can not exclude the influence of oxidation on the measured 3$d^5$ ground state configuration but the coexistence of both Mn species in the surface layer excludes that the surface layer is formed only by oxidation.
Chapter 6

Mn 3d hybridization

In this chapter the hybridization of Mn 3d with Ga/As 4sp valence orbitals is studied systematically using high resolution XAS and XMCD spectroscopy for samples with different Mn concentrations. The spectral XAS and XMCD line-shape is known to be characteristic for the electronic 3dn valence configuration \([11, 50, 51, 6, 21]\). Most models of exchange coupling presently discussed in the literature are based on a localized Mn 3dn electronic configuration which interacts with holes via impurity states consisting of mainly Ga/As 4sp orbitals \([45, 46, 44]\). Population analysis indicates that the number of Mn 3d electrons is actually between 3dn and 3d6 \([47]\). This is in agreement with experimental investigations using x-ray magnetic circular dichroism (XMCD) \([11, 21]\). However, there are also experimental reports that Mn is present in a 3d4 configuration \([61]\). In ref. \([61]\) the 3d4 component was even considered essential to establish ferromagnetic order. The presence of Mn interstitials close to clusters of substitutional Mn was theoretically predicted to strongly modify the exchange coupling between the latter as well as their charge state \([20, 49]\). Finally, in contrast to II-VI based magnetic semiconductors no antiferromagnetic exchange between Mn-Mn nearest neighbors has been considered for Ga1-xMnxAs due to a lack of experimental evidence despite its possibly adverse effect on a high ferromagnetic Tc \([2]\). Here we present experimental evidence for antiferromagnetic exchange between Mn-Mn nearest neighbors in Ga1-xMnxAs at high Mn concentrations.

6.1 Influence of the surface

As demonstrated before, using the fluorescence yield detection in XAS and XMCD is the ideal choice to probe the bulk properties of dilute Ga1-xMnxAs samples. But of course also the surface contributes to some extend to the signal. To eliminate or minimize the influence of any modified surface layer (see chapter 5) on the bulk measurements the sample surfaces were prepared by in situ Ar-ion sputtering to remove the surface layer and any contaminants. The surface preparation
Figure 6.1: A) After Ar-ion sputtering the electron yield signal (blue squares) and the fluorescence signal (black circles) of the x=0.008 sample become more similar but not identical. The corresponding XMCD spectra in B were recorded at 4K and 2.5T external magnetic field. They demonstrate that by sputtering also the contributions of the paramagnetic \( d^5 \) species to the electron yield XMCD signal are removed. The inset displays the electron yield XAS before (blue line) and after (blue squares) sputtering.
can be monitored in XAS and XMCD by total electron yield detection. Typical XAS spectra before and after sputtering are shown in the inset of Fig. 6.1 A) The 
$d^5$ multiplet (solid line in the inset) characteristic for the as grown sample (see Fig. 5.1) disappears after the surface layer is removed (blue squares in the inset). As visible in Fig. 6.1 A) the lineshape of the total electron yield spectrum (solid squares) is then similar to that of the fluorescence yield (open circles). But a distinct broadening of the electron yield XAS spectrum remains compared to the fluorescence yield data. The origin of that broadening could be due to disorder at the surface which is of course increased by the Ar-ion sputtering. Also the total electron yield XMCD signal (solid squares in Fig. 6.1 B) is broadened compared to the fluorescence XMCD signal (open circles in Fig. 6.1 B) and the surface XMCD amplitude is reduced compared to that of the bulk. For an external magnetic field of 4T the slight broadening at the high energy side of the $L_3$ peak, visible in Fig. 6.1 B), indicates the presence of paramagnetic Mn atoms which are absent in the bulk. A difference in the fluorescence yield spectra before and after removing the surface layer was only observed in case of the annealed $x=0.062$ sample where the Mn $d^5$ containing surface layer was $(5.8 \pm 0.9)$ nm thick, i.e. much thicker than in the as-grown state. In all other cases the influence of the surface layer to the bulk spectra was negligible. In the literature also HCl etching is used to remove the surface layers from Ga$_{1-x}$Mn$_x$As samples [21]. The results of this method are very similar to sputtering. Fig. 6.2 presents the electron yield spectrum of a sample prepared by HCl etching taken from ref. [21] (red line) compared to that of a sputtered sample (blue squares). Both spectra are identical indicating the same influence of disorder. This underlines the advantage of the fluorescence signal probing the undisturbed bulk properties.

6.2 $pd$-hybridization of ferromagnetically coupled Mn

Typical Mn $L_{3,2}$ XAS and XMCD spectra for two different Mn concentrations, the $x=0.008$ sample (black line) and the $x=0.062$ sample after annealing (red line) are shown in Fig. 6.3 A) and b), respectively. The spectra were recorded at 10K with saturation magnetic fields (see Fig. 6.5) of 4.5T ($x=0.008$) and 2.5T ($x=0.062$) applied along one of the two equivalent in-plane hard magnetic $<110>$ axes. The spectra are normalized to a constant step like background caused by transitions into continuum states. The observed XMCD lineshape is identical to the one reported previously [11, 21, 17]. Only the as-grown $x=0.062$ XMCD spectrum (green line in the inset of Fig. 6.3 B)) displays lineshape changes which, however, disappear after interstitial Mn atoms are removed by annealing (see red line in the inset of Fig. 6.3 B)).

At low Mn concentrations of $x=0.008$ and $x=0.017$ (not displayed in Fig. 6.3)
Figure 6.2: Samples prepared by Ar sputtering (blue squares) and by HCl etching (red line) have almost identical surface XAS (electron yield) spectra. The spectrum of the HCl etched sample was digitized from ref. [21] and stems from a sample with almost the same Mn concentration ($x=0.067$) as the sputtered sample ($x=0.062$) studied in this work.
Figure 6.3: XAS (A) and XMCD (B) spectra of the $x=0.008$ (black line) and the $x=0.062$ sample after annealing in vacuum (red symbols). The XMCD lineshape of the as grown $x=0.062$ sample (green symbols) is shown in the inset. The spectra were recorded at 10K for an incidence angle of 20° relative to the sample surface with the photodiode positioned at 90° relative to the incident x-rays.
there is excellent agreement between the experimentally observed lineshape and Anderson impurity calculations [51] of the XAS [21] and XMCD [11] spectra. A comparison between the calculated XAS [21] and XMCD [11] spectra (red line) and the measured spectra for the x=0.008 sample (open circles) is shown in Fig. 6.4 A) and B), respectively. The Mn 3d electronic configuration fluctuates mainly between 3d⁵ and 3d⁶ with an average 3d electron count at all Mn sites near n=5.1 [21] or 5.2 [11]. We note that the XAS and XMCD lineshapes cannot be reproduced by an incoherent superposition of 3d⁵ and 3d⁶ configurations [51]. This implies that all Mn atoms have the same mixed valence 3d⁵-3d⁶ ground state and there is no phase separation e.g. in 3d⁵ and 3d⁶-like Mn sites.

However, at higher Mn concentrations the asymmetric broadening of the XAS lineshape (red line in Fig. 6.3) indicates that there is more than one Mn species present. Whereas the unaltered XMCD lineshape present in all samples demonstrates that the Mn 3d valency is intimately linked to the observed exchange coupling in Ga₁₋ₓMnₓAs. Only a mixed valence Mn 3d⁵-3d⁶ ground state is responsible for ferromagnetic coupling at all Mn concentrations! Obviously the second species of Mn atoms with a different 3d configuration contributes only to the asymmetrically broadened XAS lineshape at x=0.062 but not to the XMCD spectrum. This is only possible if the second species is non-ferromagnetic. Please note that this lineshape change cannot be caused by a phase separation and the formation of MnAs clusters as reported in ref. [48]. MnAs is known to display a large chemical shift and a significantly different lineshape than the one observed in Fig. 6.3 [16].

6.3 Saturation magnetization

The XMCD intensity depends strongly on Mn concentration and annealing. This can be seen by the magnetization curves displayed in Fig. 6.5. The magnetization curves were recorded by the XMCD signal on the L₃ peak at a sample temperature of 10K. For x=0.008 sample (black symbols) and the 0.018 (magenta symbols) the magnetization curves show signs of coexisting ferromagnetic and paramagnetic regions. With increasing Mn concentration Tₐ increases and the ferromagnetic regions develop into percolation networks eventually covering the whole sample at x=0.062. This behavior is also reflected in an increase of XMCD intensity with x at remanence as observed previously [17]. The saturation magnetization for the different samples can be obtained directly from the magnetization curves. Before evaluating the XMCD signal at the L₃ peak all spectra have been normalized to a constant step edge. For the x=0.008 and the x=0.017 samples (black and magenta line in Fig. 6.5) the saturated XMCD signal reaches at the L₃ peak an value of 65% asymmetry, i.e. the difference of the two XAS spectra recorded with opposite x-ray helicity divided by the sum of both. Following the calculations of ref. [11] such dichroic asymmetry corresponds to fully aligned Mn magnetic
Figure 6.4: XAS (A) and XMCD (B) spectra of the x=0.008 (open circles) compared to Anderson impurity calculations [51] of the XAS [21] and XMCD [11] assuming a Mn 3d electronic 3d\(^5\) configuration with an admixture of 3d\(^6\) contributions. The average 3d electron count at all Mn sites was set to n=5.1 [21] or 5.2 [11] (red line).
moments with an average magnetic moment of $4.6\mu_B$ per Mn atom [11]. The average magnetic moment per Mn atom in saturation for the $x=0.062$ sample is significantly reduced in the as grown state (green lines) and the 24h annealing in vacuum reduced it even further as can be seen by the red line in Fig. 6.5. The inset in Fig. 6.5 demonstrates that the concentration dependent XMCD reduction at saturation (orange symbols) scales approximately with the calculated number of Mn atoms that have a Mn nearest neighbor (blue symbols).

### 6.4 Evidence for antiferromagnetic coupling of Mn

It is very likely that the reduced saturation magnetization observed in the $x=0.062$ sample and the asymmetric broadening of its XAS lineshape have the same origin. As shown in Fig. 6.6 after annealing of the $x=0.062$ sample the saturation magnetization is reduced further. This is accompanied by a stronger asymmetric broadening of the XAS lineshape. This effect is clearly visible at the low photon energy side of the $L_3$ peak enlarged in the inset of Fig. 6.6. The easiest explanation of the observed effect would be that the asymmetric broadening is caused by an admixture of non-ferromagnetic Mn that leads to the observed reduction in the average magnetic moment per Mn atom. This would mean that the XAS spectrum of the $x=0.062$ sample can be decomposed into a ferromagnetic species with a lineshape identical to the XAS spectrum for the $x=0.008$ sample according to the observed XMCD intensity. The remaining part of the spectrum would be characteristic for the non-ferromagnetic species. Such a decomposition of the XAS spectra for the $x=0.062$ sample into spectra for non-ferromagnetic (red symbols and green symbols) and ferromagnetic Mn species (black lines) is shown in Fig. 6.7. The lineshape of the XAS spectrum for the ferromagnetic species was assumed to be identical to that for $x=0.008$. Its intensity was rescaled according to the measured XMCD ratios for $x=0.008$ and $x=0.062$ as shown in the inset (black line). This corresponds to the fraction of ferromagnetically aligned Mn atoms in the sample. The lineshapes of the resulting XAS spectra of the non-ferromagnetic Mn species for as-grown (green symbols) and annealed (red symbols) $x=0.062$ sample are identical. This lends credibility to the quality of the decomposition procedure.

The observed XAS lineshape displays much less pronounced multiplet features than that of the ferromagnetic species. Such an effect is characteristic for increased valence electron fluctuations [50, 51] possibly due to increased electronic hopping between $3d$ shells of adjacent Mn-Mn pairs. A detailed lineshape analysis similar to the $3d^5$-$3d^6$ Mn species is not available yet. However, information about the ground state properties can be extracted using the integral XAS intensities after subtracting a step like background [50] shown in Fig. 6.7 B).
Figure 6.5: The XMCD signal at a photon energy of 640eV is used to probe the sample magnetization versus applied magnetic field for as-grown (Ga$_{1-x}$Mn$_x$)As samples with $x=0.008$, 0.017 and 0.062 (solid black, solid magenta, and solid green symbols). The magnetization curve for the annealed $x=0.062$ sample is displayed by open red symbols. All spectra were taken at 10K which is only slightly below $T_C$ for the $x=0.008$ sample. The upper inset shows the relative saturation magnetization, $M_{sat}$ (orange symbols) and the calculated number of Mn atoms that have nearest neighbors, $N_{Mn-Mn}$, (blue symbols) vs $x$. 

6.4 Evidence for antiferromagnetic coupling of Mn
Figure 6.6: The bulk XAS and XMCD spectra of the $x=0.008$ sample (black line) are compared to those of the $x=0.062$ sample at different stages of annealing: as grown (green) and after annealing under vacuum (red). As demonstrated in A) the XAS lineshapes are not identical, especially at the low energy side of the $L_3$ peak (enlarged in the inset) differences between the $x=0.008$ sample (black line) and the $x=0.062$ (red symbols) are obvious. The saturation magnetization of the $x = 0,062$ sample annealed under vacuum is reduced by a factor of 0.54 compared the $x=0.008$ sample, but the XMCD lineshapes of both are exactly identical as demonstrated in B). The inset in A) visualizes how the XAS lineshape of the $x = 0,062$ sample varies with the stage of annealing. This corresponds to a change of the saturation magnetization that is shown in the inset of B). The XAS and XMCD spectra of the $x=0.017$ sample (not shown) were identical to the $x=0.008$ case.
Figure 6.7: A) XAS spectra representing ferromagnetic (black line) and non-ferromagnetic Mn species for as-grown (green symbols) and in vacuum annealed $x=0.062$ (red symbols). The inset illustrates the decomposition of the annealed $x=0.062$ XAS spectrum (red line) as described in the text. B) Integral of the XAS spectra in A) after subtraction of a step like background [50]. The integral intensity corresponds to the number of unoccupied Mn 3$d$ states for the respective species.
Sum rules relate the total $L_{3,2}$ intensity to the average number of unoccupied 3d levels, $n_h=10-n$ \cite{51, 50, 11, 21}. For the non-ferromagnetic species we find a 20\% reduced 3d electron count close to $3d^4$ compared to that of ferromagnetic Mn atoms. Even if the lineshape in Fig. 6.7 A) shows that this is not a pure atomic $3d^4$ configuration \cite{51}. Interestingly there is hardly a change in the branching ratio, $BR=I(L_{3})/[I(L_{3})+I(L_{2})]$, of the integral $L_{3,2}$ intensities, $I(L_{3,2})$. We find BR values of 0.72±0.01 and 0.75±0.01 for the ferromagnetic and non-ferromagnetic Mn species, respectively. Branching ratios so much larger than the statistical value of 2/3 are typical for high-spin ground state configurations \cite{65, 50}. This result together with the zero XMCD spectrum is conclusive evidence that the $3d^4$-like Mn species is present as clusters of two or more Mn atoms with their high-spin atomic magnetic moments compensated by antiferromagnetic coupling.

6.5 Discussion

The concentration dependent XMCD reduction scales approximately with the calculated number of Mn atoms that have a Mn nearest neighbor (blue symbols in the upper inset of Fig. 6.5). The observed XMCD lineshape is characteristic for a high-spin $3d^5$ ground state configuration with a small $3d^6$ admixture \cite{11}. The characteristic $3d^5$ atomic multiplet is still discernible as peaks in the XMCD and the XAS spectra of Fig. 6.6 \cite{51} but the structures are attenuated by the $3d^6$ ground state weight \cite{11, 21}. The latter is caused by hybridization of Mn 3d and ligand Ga/As 4sp-states. It is characterized by an extra Mn 3d electron and a hole on the ligand atoms. Delocalized ligand holes mediate the ferromagnetic exchange between localized Mn impurities in dilute magnetic semiconductors \cite{2}. For a high-spin $3d^5$ configuration only an extra electron with opposite spin orientation can be accommodated \cite{50}. Therefore, the $3d^6$ weight leads to antiferromagnetic alignment between Mn and As magnetic moments as observed in ref. \cite{17}. The mixed valence $3d^5$-$3d^6$ configuration is characterized by an average number of $n=5.2$ Mn 3d electrons on all sites \cite{11}. Similar values of $n=5.3$ and 5.1 were obtained from photoemission measurements and cluster model calculations \cite{53} and XAS data (see below) \cite{21}. The unaltered XMCD lineshape at all Mn concentrations demonstrates an identical local Mn 3d electronic configuration of the ferromagnetic Mn species \cite{11, 50}. It also implies that the local magnetic moments are identical for the ferromagnetic Mn species at all concentrations. Together with the reduced XMCD signal at saturation this shows that the fraction of Mn atoms participating in the long-range ferromagnetic order is reduced at larger concentrations. Part of this effect could be caused by non-collinear arrangements of Mn magnetic moments due to a RKKY-like magnetic interaction \cite{46}. However, since the Mn XMCD lineshape is known to be very sensitive to changes in the magnetic exchange coupling \cite{50} the latter effect should play a minor role. The presence of Mn interstitials in the as-grown $x=0.062$ sample
causes a slightly different XMCD lineshape. This is a strong indication that substitutional and interstitial Mn occupy neighbor sites and form magnetic clusters [49, 10].

Ferromagnetism is connected only to the $d^5$-$d^6$ Mn species as, for instance, evidenced by the temperature dependent hysteresis loop changes in Fig. 6.5. In this case the exchange of holes mediates ferromagnetic coupling and long range ferromagnetic order sets in as the Mn concentration increases [45, 46, 49]. On average there is much less than one hole per ferromagnetic Mn acceptor [2, 45, 20]. Theoretical models indicate that compensation of the negative charge for neighboring Mn-Mn acceptor pairs by up to two holes can lead to antiferromagnetic interaction between Mn neighbors [20]. It is tempting to explain the identified antiferromagnetic $d^4$-like Mn clusters by this scenario. The observed increase in the number of $d^4$-like Mn atoms by removal of Mn interstitials is in agreement with first principles calculations which predict interstitial Mn to cluster with two or more substitutional Mn atoms [49]. This proximity of interstitial and substitutional Mn is also thought to affect the ferromagnetic coupling between the latter [49]. We surmise that this could explain the observed 10% change in Mn magnetization upon the removal of 5% Mn interstitials (described in the previous chapter). We can presently only speculate that the electric charge of substitutional Mn-Mn acceptor clusters might be screened by valence holes. The results could then indicate that some of these holes are tightly bound around antiferromagnetic Mn-Mn pairs and may even hop onto the Mn 3$d$ shell as reflected in the experimentally observed 20% reduced Mn 3$d$ electron count for this species. It will be interesting to see a first-principles description of such an effect develop in the future.

6.6 Conclusion

The signature of Mn 3$d^5$-3$d^6$ mixed valence acceptor states, responsible for long-range ferromagnetic order, was identified with x-ray magnetic circular dichroism at all Mn concentrations. With increasing Mn content an increasing amount of Mn atoms is observed exhibiting a significantly reduced number of 3$d$ electrons of close to 3$d^4$. Their number scales approximately with the number of Mn nearest neighbor pairs expected for a statistical Mn distribution. Both observations can be explained by the presence of Mn-Mn nearest neighbor pairs. We also find a corresponding reduction of the number of ferromagnetic Mn atoms at high Mn concentrations. Contrary to II-VI based materials this represents the first observation of antiferromagnetic order in III-V dilute magnetic semiconductors with possibly a similar adverse effect to the ferromagnetic ordering temperature.
Mn 3d hybridization
Chapter 7

Orbital magnetic moment anisotropy

7.1 Introduction

The local exchange coupling between the GaAs valence states and the Mn $d$ states is very important for the understanding of the long range ferromagnetic coupling in Ga$_{1-x}$Mn$_x$As. The valence holes are exchange coupled to the Mn impurity $3d$ spins by $pd$-hybridization. In this chapter we present angle dependent XMCD measurements that show a variation of the Mn $3d$ orbital moment with the in-plane azimuthal lattice direction. Correlated spectroscopic lineshape changes in the XMCD spectra can be interpreted as an anisotropy in the spatial overlap of Mn $3d$ and As $4sp$ states that is probed by the spin-orbit coupling, present in the Mn $3d$ shell. This interpretation is in agreement with recent calculations predicting a strongly anisotropic $pd$-hybridization [71]. This is the first experimental evidence for an orientation dependent $pd$-hybridization in Ga$_{1-x}$Mn$_x$As.

7.2 Results

7.2.1 Orbital magnetic moment anisotropy

In this chapter we will focus on the annealed sample with $x=0.062$. At low temperature (5-10K) this sample exhibits two in-plane easy-axis of the magnetization which are oriented along the equivalent $<100>$ lattice directions as determined by SQUID measurements [68]. Analyzing the magnetization by XMCD spectroscopy we find an obvious difference between XMCD spectra that were recorded with the magnetization aligned along the equivalent $<100>$ and the equivalent $<110>$ lattice directions. The Fig. 7.1 B) shows two XMCD spectra that were recorded in magnetic saturation with an external magnetic field of 4T applied. For the red spectrum the magnetic field and the incoming x-ray
Figure 7.1: This figure displays spectra of the annealed $x=0.062$ sample recorded at 5K and an incidence angle of $20^\circ$ relative to the surface. In panel B) two XMCD spectra are displayed: for the red XMCD spectrum the magnetization was saturated along a hard magnetic $<110>$ axis whereas the black spectrum was recorded with the magnetization saturated along an easy magnetic $<100>$ axis. The integrals over the XMCD spectra are shown as dashed lines. Panel A) shows the corresponding isotropic XAS spectra (solid lines) and their integrals (dashed lines) after subtraction of the indicated step function (dotted line). Only the XAS spectra were normalized to an identical height of the step edge.
beam were aligned along the $<110>$ lattice direction (hard axis) whereas for the black XMCD spectrum the azimuth of the sample was rotated by $45^\circ$ so that the magnetization was aligned along the $<100>$ direction (easy axis). The incidence angle was in both cases $20^\circ$ and the sample temperature $5K$.

By sum rule analysis (see chapter 2) we find for both directions a non-zero orbital moment residing on the Mn $3d$ shell. In both cases the orbital moment is positive, which means that spin and orbital moment are aligned parallel. According to Hund’s rule this is expected for a more than half filled $3d$ shell and agrees very well with a $d^5$ admixture to the mainly $d^5$ ground state (see chapter 2). As described in chapter 2 only the $d^5$ contribution carries an orbital moment which is zero for a high-spin $d^5$ configuration. Our experimental data demonstrate that the size of the orbital moment strongly depends along which axis the magnetization is aligned. The absolute orbital moments were calculated using equation 2.14. Where the occupation of the $d$-shell was assumed to be 5.2 electrons as determined from the ground state hybridization analysis in chapter 6. From the integrated XMCD and XAS spectra shown in Fig. 7.1 we obtain orbital moments of $0.02 \pm 0.01 \mu_B$ per Mn atom if the magnetization is aligned along the easy axis which is significantly lower than the value of $0.055 \pm 0.01 \mu_B$ obtained for the magnetization aligned along the hard axis. This is in contradiction with an increased orbital moment along the easy axis as described by Bruno’s model due to magneto crystalline anisotropy [56]. This contradiction points to a different origin of the orbital moment anisotropy. In the next section we will demonstrate that the orbital magnetic moment anisotropy is correlated to clear differences in the XMCD lineshape. The two observed XMCD lineshapes provide a direct access to a different ground state hybridization.

### 7.2.2 Angular dependence the of ground state hybridization

The XMCD lineshapes measured with the magnetization saturated along the $<110>$ lattice directions (red line) and the $<100>$ lattice directions (black line) are different. This is shown in Fig. 7.2. The insets show enlarged regions of the spectra with the distinct lineshape changes. The two XMCD spectra were not scaled relative to each other. They match each other perfectly except for the regions enlarged in the insets. Inset a) shows that the small positive peak at the high energy side of the negative XMCD $L_3$ main peak is increased if the magnetization is saturated along a $<100>$ lattice direction. In this configuration also the low energy side of the $L_2$ doublet is increased in combination with a sharpening of the rising edge as shown in the inset b).

Fig. 7.3 A) demonstrates that this effect depends only on the alignment of the magnetization and is not due to any artifact introduced by the sample rotation. The figure shows two XMCD spectra measured along the $<110>$ hard
Figure 7.2: A) This figure compares XMCD spectra of the annealed $x=0.062$ sample recorded at 5K and 4T magnetic field applied along two different lattice directions to calculated XMCD spectra. For the red XMCD spectrum displayed in panel A) the magnetization was saturated along a $<110>$ direction (hard magnetic axis) whereas the black spectrum was recorded with the magnetization saturated along a $<100>$ direction (easy magnetic axis). The insets enlarge parts of the two spectra which exhibit lineshape variations. The XMCD spectra displayed in panel B) were calculated for a pure Mn $3d^5$ configuration (blue line) and for a Mn $3d^5$ configuration with an admixture of $3d^6$ (magenta line) (taken from [51, 11])
magnetization direction. The spectra are normalized to equal XMCD intensity at the negative $L_3$ peak. In remanence, i.e. with no external magnetic field applied, the spectrum (black line) corresponds to that with the spins aligned along the easy $<100>$ and equivalent directions, although attenuated by the incomplete alignment of x-ray polarization and magnetization direction. In an applied magnetic field of 2.5T (red line) the spins rotate into the hard $<110>$ direction. The spectra in Fig. 7.3 A) are identical to the one shown in Fig. 7.2 A) with the same lineshape changes. However this procedure of forcing the spins away from the easy direction gives far more accurate results and it is, for instance, possible now to study the temperature dependence of the lineshape changes. This is shown in Fig. 7.3 B) where the difference spectra of the XMCD data of Fig. 7.3 A) are displayed together with spectra measured at elevated temperatures of 15K (green line) and 50K (black line). The integrals over the spectra are shown in the inset. The effect decreases rapidly with the temperature and is very small at 50K which is 22K below the critical temperature.

Unfortunately no calculations have been carried out so far to reproduce these XMCD lineshape variations. For a qualitative evaluation we can compare the observed XMCD lineshapes to the calculated XMCD spectra for a pure $d^5$ ground state [51] (blue line) and the hybridized ground state of 80% $d^5$ with a 20% $d^6$ admixture [11] (magenta line) shown in Fig. 7.2 B). The regions enlarged in the insets a) and b) are the same as in panel A). Comparing the enlarged regions in panels A) and B) we find obvious similarities that allow us to correlate the change in the measured XMCD lineshape with a trend in the ground state hybridization. The stronger positive peak in inset a) and the sharp rise at the onset of the $L_2$ edge shown in inset b) are obviously fingerprints of a more localized $3d^5$ configuration with less admixture of a $d^6$ configuration. In this simplifying and qualitative picture the Mn $3d$ ground state turns out to be less hybridized with the GaAs $sp$ orbitals if the magnetization is aligned along the easy axis.

Finally it should be noted that these changes are obvious only in the XMCD signal. Within the experimental error the isotropic lineshape does not depend on the magnetization orientation. Thus the XMCD lineshape is either much more sensitive to changes in the Mn $3d$ ground state hybridization than the isotropic XAS spectrum or the total $3d$ electron count and, therefore, the charge transfer between the Mn $d$ orbitals and the As ligands does not change with the orientation of the magnetization vector.

7.3 Discussion and conclusions

We have shown above that the XMCD lineshape varies if the magnetization is saturated along an easy ($<100>$) or hard magnetic ($<110>$) axis. Analyzing the two different XMCD lineshapes in a simplified way we obtained qualitative information about the corresponding ground state configurations. With the
Figure 7.3: A) XMCD lineshape of the $x=0.062$ sample recorded at two different magnetic fields of 2.5T (red line) and 0.01T (black line) applied along the $<110>$ direction (hard axis). The spectra are scaled to identical amplitude at the L$_3$ edge. The difference of the two XMCD spectra is displayed in B) for temperatures of 5K (blue line), 15K (green line) and 50K (magenta line). The inset displays the integral of the difference spectra.
magnetization oriented along an easy axis the XMCD lineshape indicates a more localized $d^5$ like configuration whereas for the magnetization aligned along a hard axis the corresponding ground state configuration appears to be more hybridized i.e. it shows stronger mixing of $d^5$ and $d^6$ configurations. Evaluating the orbital moment with sum rules we found that the change in the XMCD lineshape is correlated with a change in the orbital moment. Surprisingly for the magnetization aligned along the hard magnetic axis the orbital moment is found to be larger than for an alignment along the easy axis. From that observation it can be excluded that the anisotropy of the orbital magnetic moment is caused by magneto-crystalline anisotropy effects which should result in a different variation of the orbital moment. To understand the observed effect it is important to consider the Mn 3$d$ orbitals involved in the $pd$-hybridization. The Mn 3$d$ levels are split by the tetrahedral crystal field into an $E$-symmetric doublet and a $T_2$-symmetric triplet [69]. Fully occupied $t_{2g}$ and $e_g$ states inside the valence band have mainly Mn $d$ character whereas the partially filled $t_{2g}$ states at the valence band are formed of Mn 3$d$ and As $p$ orbitals [71]. The absolute values of the $t_{2g}$ wave functions are shown in Fig. 7.4. Assuming spin conserving hopping interactions between those partially occupied orbitals the exchange interaction $J_{ij}(R)$ between Mn pairs at the distance $R$ along different lattice orientations has been studied [71]. In contrast to RKKY calculations assuming a spherical $pd$-hybridization the exchange intensities were found to depend on the specific lattice orientation [71]. A scheme of the $t_{2g}$ energy levels of two interacting Mn atoms is given at the top of Fig. 7.5. Spin-up and spin-down states of the Mn atoms interact by spin conserving hopping and form a set for bonding and antibonding states. The results of the ab initio total energy calculations are shown in the lower panel of Fig. 7.5. The ferromagnetic stabilization energy $E_{AFM} - E_{FM}$ is found to be highest if the hopping interaction occurs along the $<110>$ lattice direction [71]. Calculations using large cells of up to 256 atoms could demonstrate a significant domination of the orientation dependence over the distance dependence in the exchange coupling [71]. The exchange coupling of Mn pairs oriented along the $<110>$ axis.

Figure 7.4: Absolute values of the Mn 3$d$ $t_{2g}$ wave functions in respect to the crystallographic axes. Open circles indicate the As ligands of the central Mn atom.
remains higher in strength compared to Mn pairs oriented along other directions even if their separation $\mathbf{R}$ is smaller [71]. In the previous chapters it has been demonstrated that the $pd$-hybridization introduces a 20% $d^6$ admixture to the Mn $3d^5$ ground which is characteristic for substitutional Mn. This admixture of $d^6$ is also the origin of the orbital magnetic moment residing on the Mn $3d$ shell (a pure $d^5$ high-spin state is spherically symmetric and possesses no orbital moment). The angular dependence of the orbital moment and the change in the ground state hybridization indicated by the XMCD lineshape are obviously not due to magneto-crystalline anisotropy but reflect the spatial anisotropy of the hybridization between Mn $d$ states and the dangling $sp^3$ hybrids of neighboring As atoms. The ab initio total energy calculations based on $pd$-hopping interactions predicted that a significant feature of the $J_{ij}$ exchange-coupling strength is a pronounced orientation dependence [71]. Dominant contributions stabilizing the ferromagnetic state are maximal along the $<110>$ directions and minimal along the $<100>$ directions i.e. the hopping strength along the $<110>$ direction is found to be larger than along the $<100>$ direction. It is tempting to correlate this predicted anisotropy of the $pd$-hybridization with the directional dependence of the $d^6$ ground state weight observed in XMCD. As an effect of the Mn $3d$ spin-orbit coupling XMCD, therefore, is sensitive to the directional dependence of valence fluctuations. In agreement with the preferred hopping along the $<110>$ directions we observe the higher XMCD $d^6$ ground state weight along this direction.

The conclusion of the above described effect is that due to the spin-orbit coupling in the Mn $3d$ shell XMCD spectroscopy is able to map the spatial anisotropy of the $pd$-hybridization in Ga$_{1-x}$Mn$_x$As. By XMCD spectroscopy we can identify distinct spectroscopic features that are related to the spatial overlap of Mn $3d$ and As $sp$ states influencing the ferromagnetic ordering. This is exactly what is needed for a detailed understanding of the origin of ferromagnetism in these systems. In future this effect could be used to test theoretical models.

### 7.4 Outlook

So far we studied the effect of the anisotropic $pd$-hybridization on the XMCD lineshape by changing the orientation of the magnetization axis. Within the experimental uncertainty the isotropic XAS signal was not affected by that. This indicates that we probe the anisotropy of the $pd$-hybridization via the spin-orbit interaction but the charge transfer between the Mn $d$ orbitals and the As ligands does not change with the magnetization direction or the changes are too small to be resolved in our experiment. As an outlook on future projects we present data that possibly indicate changes in the charge transfer between the Mn $d$ orbitals and the As ligands occurring between the ferromagnetic state at low temperature and an non ferromagnetic state above the critical temperature. The
Figure 7.5: A) Schematic energy levels for two interacting Mn atoms with their spins ferromagnetically and antiferromagnetically aligned. B) Distance and orientation dependence of $E_{FM}$ and $E_{AFM}$ for two Mn atoms in a 64 atom GaAs cell obtained by ab initio total energy calculations. The direction of the vector connecting the two Mn atoms is given by the upper x-axis. (both taken from [71])
data were recorded on the x=0.017 sample which exhibited the same anisotropy and the same the dependence of the XMCD lineshape on the magnetization axis but less pronounced than the x=0.062 sample. In Fig. 7.6 A) the isotropic XAS of the x=0.017 spectrum is displayed and in Fig. 7.6 C) the difference of two XMCD spectra comparable to that in Fig. 7.3 is shown. As for the x=0.062 sample one XMCD spectrum was recorded in remanence and the other one with 4T magnetic field applied along the hard axis. Prior to subtraction both spectra were normalized to identical L₃ peak height. The shown XAS data are the average of more than fifty single spectra, thus we could reduce the noise to less 0.5 permil of the peak intensity. The interesting result is, that the isotropic XAS spectrum recorded at 5K differs from XAS spectra recorded at 40K which is above the critical temperature. The difference of these two XAS spectra (high minus low temperature) is shown in Fig. 7.6 B). It was of course tested that these minimal variations can not originate from a small energy shift between the two spectra. Most interestingly the changes in the XAS intensity occur mainly at positions of the spectrum where the XMCD lineshape was found to be sensitive to the spatial structure of the pd-hybridization. This coincidence makes it possible that the observed changes in the XAS lineshape reflect a general change pd-hybridization at the onset of ferromagnetism. By the positive integral of the difference spectrum shown as a dashed line in Fig. 7.6 B) we can determine that the number of d holes is larger at 40K than at 5K. This would mean that the charge transfer between the Mn d orbitals and the ligands is reduced above the critical temperature. It will be the purpose of future projects to study these promising observations in more detail.
Figure 7.6: This figure displays spectra of the x=0.017 sample normalized to the mirror current without any self absorption correction. A) XAS spectrum recorded at 5K. B) Difference of two XAS spectra recorded below and above the Curie temperature (40K - 5K). The integral of the difference is shown as a dashed line. C) Difference of two XMCD spectra recorded in remanence (0.01T) and in saturation (4T) both at 5K.
Orbital magnetic moment anisotropy
Chapter 8

Summary

In the recent years a large field of research emerged, exploring the possibilities how to introduce and handle spin polarized carriers in semiconductor materials. One of the goals is to incorporate spintronic devices in conventional semiconductor technology. Very promising systems are the dilute magnetic semiconductors, where the spin polarized carriers arise from magnetic ions doped into the semiconductor host.

In this thesis we studied the origin of the ferromagnetic ordering in Ga$_{1-x}$Mn$_x$As, the most prominent member of the III – V series of ferromagnetic DMS. The ferromagnetism in Ga$_{1-x}$Mn$_x$As is based on two cooperative effects, caused by replacing the trivalent Ga atoms with Mn. Mn provides a local spin magnetic moment and as an acceptor it creates itinerant holes, which mediate the long range ferromagnetic order [1]. But the limited solubility of Mn can lead to a high number of defects e.g. As antisites and interstitial Mn [4]. Due to the complexity of Ga$_{1-x}$Mn$_x$As and the high degree of disorder, the physics underlying its magnetic properties is still under discussion, even if various theoretical models exist [2, 3]. For further understanding of the ferromagnetic ordering the electronic configuration of the Mn impurities and the number of Mn atoms contributing to the long range ferromagnetic order are of major interest. We probed these parameters directly by x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD). The spectral XAS and XMCD lineshape is known to be characteristic for the electronic 3$d^n$ valence configuration [11, 50, 51, 52, 21].

In contrast to previous attempts we combined surface and bulk sensitive detection methods with additional reflectivity measurements to resolve a chemical and magnetical depth profile of the (GaMn)As layer. This analysis revealed the presence of two different Mn species with different XAS and XMCD line shapes in our samples. The bulk of the Ga$_{1-x}$Mn$_x$As samples is dominated by substitutional Mn residing at the Ga sites. This species can easily be identified by its ferromagnetic properties and a mixed valence 3$d^5$ - 3$d^6$ electronic configuration which is characteristic for the hybridization with GaAs valence orbitals. At the surface we find an accumulation of non-ferromagnetic Mn in a 3$d^5$ elec-
tronics configuration. The enhanced surface segregation of this second Mn species upon annealing, causing a large surface magnetization deficit of substitutional Mn, provides strong evidence that the second Mn species is related to interstitial Mn. Acting as a double donor interstitial Mn should strongly reduce the carrier density and, therefore, also the ferromagnetic coupling between substitutional Mn. Our results demonstrate that XAS and XMCD spectra representing the bulk properties of Ga$_{1-x}$Mn$_x$As can only be obtained if the influence of the surface layer is excluded.

Using the bulk sensitive XAS and XMCD spectra we studied the hybridization of Mn 3$d$ with GaAs 4$sp$ valence orbitals systematically for samples with different Mn concentrations. We find a signature of Mn 3$d^5$-3$d^6$ mixed valence acceptor states responsible for long-range ferromagnetic order at all Mn concentrations. This is in agreement with previous experimental investigations [11, 81] and with theoretical models based on a localized Mn 3$d^5$ electronic configuration which interacts with holes via impurity states, consisting of mainly GaAs 4$sp$ orbitals [45, 46, 44]. In addition we find experimental evidence for an antiferromagnetic exchange between Mn-Mn nearest neighbors in (GaMn)As at high Mn concentrations. With increasing Mn concentration an increasing amount of Mn atoms not participating in the ferromagnetic ordering is observed. Their number scales approximately with the number of Mn nearest neighbor pairs expected for a statistical Mn distribution. For the Mn atoms not participating in the ferromagnetic ordering we also find a reduced number of 3$d$ electrons of close to 3$d^4$. Both observations can be explained by the presence of Mn-Mn nearest neighbor pairs. It has been predicted theoretically that the exchange coupling and the charge state of Mn in clusters of substitutional Mn can be strongly modified by the presence of interstitial Mn [20, 49]. Contrary to II-VI based materials this represents the first observation of antiferromagnetic order in III-V dilute magnetic semiconductors with possibly a similar adverse effect to the ferromagnetic ordering temperature.

In angle resolved XMCD measurements we studied the hybridization of the Mn 3$d$ shell with GaAs valence orbitals. The $pd$-hybridization is usually assumed to be spherically isotropic [2]. But we find a variation of the Mn 3$d$ orbital moment with the in-plane azimuthal lattice direction that is correlated with distinct spectroscopic features. The observed dependence of the orbital magnetic moment on the lattice directions is contrary to what is expected from the magneto crystalline anisotropy contribution. Thus the magneto crystalline anisotropy can be ruled out to cause this effect. The spectroscopic features in the XMCD spectra and the correlated change in the orbital moment can be interpreted by an anisotropy in the spatial overlap of Mn 3$d$ and As 4$sp$ states influencing the ferromagnetic ordering. This interpretation is in agreement with recent calculations predicting a strongly anisotropic $pd$-hybridization [71]. This is the first experimental indication for an anisotropic $pd$-hybridization in (GaMn)As and, therefore, magnetic exchange coupling. The spectroscopic features related with
this effect could be used in future to test theoretical models.
Bibliography


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