Micro-scale Nuclear Magnetic Resonance on III-V Semiconductors
and the Advance of Mechanically Detected NMR

Proefschrift

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Acknowledgements

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## Notations

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Chapter 1

Nuclear Magnetic Resonance

1.1 Introduction

Nuclear Magnetic Resonance (NMR) has become a well established spectroscopic technique to obtain structural and dynamical information at the atomic/molecular level in a wide range of materials. The exciting versatility of NMR has been demonstrated over the last 70 years, but research in this area is still ongoing with great prospects. NMR was first observed with molecular beams by Rabi in 1938, for which he received the Nobel prize. In 1946 Bloch and Purcell applied the technique to liquids and solids, for which they received the Nobel prize in 1952. In 1991 Richard R. Ernst received the Nobel prize for his contributions to the development of the methodology of high resolution NMR spectroscopy. In 2002, Kurt Wuthrich was awarded for his development of NMR spectroscopy for determination of the three-dimensional structure of biological macromolecules in solution and in 2003 Peter Mansfield and Paul Lauterbur received the Nobel prize in physiology or medicine for their discoveries using gradients in the magnetic fields in Magnetic Resonance Imaging (MRI).

1.2 Ordering in semiconductors

The main part of the solid-state NMR studies presented here concerns the atomic ordering of III-V semiconductors. These types of semiconductors are grown with the elements of groups III and V of the periodic table. It is important to analyze the lattice structure of these semiconductors since their performance might be improved using knowledge about their ordering. From roughly 1950 onwards, different types of ordering were found in various III-V semiconductors, by using a wide range of spectroscopic techniques[1]. In general, the composition of III-V semiconductors is difficult to describe since various structural features can exist (simultaneously) at different length scales. For instance, the presence of both ordered and disordered domains makes it hard to analyze these structures in detail. The degree of order will affect many physical and electronic properties such as
electronic transport, mobility, thermodynamic stability and electro-optical properties. Considering the limited number of reports on long-range order in AlGaAs thin films as studied by diffraction techniques, whereas specific ordered structures are seen in a number of microscopic observations, it is interesting to study these materials with a complimentary method such as solid-state NMR. As NMR probes short-range order, the presence of locally occurring structures can be detected if present in sufficiently high concentrations. Since the NMR signal is composed of contributions from the entire sample, the possibility that one is studying a specific anomaly is reduced. Long-range ordered structures will result in a specific signature which can be directly distinguished from a disordered structure.

In Chapter 2 thin film powdered Al$_x$Ga$_{1-x}$As samples were studied with NMR techniques such as QCPMG, Hahn-echoes, mutation and MQMAS of different nuclei Al, Ga and As. Five sites of Al$_n$Ga$_{4-n}$As ($n = 0 \ldots 4$) were identified in the $^{75}$As spectra, each site having specific spectroscopical features. Electronic structure calculations were carried out to model the quadrupolar interaction parameters and match these to the different cation configurations. However, because of the powder nature of the sample, the quadrupolar features were smeared out over a very large spectral range.

In Chapter 3 a thin film Al$_{0.5}$Ga$_{0.5}$As sample was analyzed using a flat strip-line radio-frequent resonator. The presence of only a distinct number of relatively sharp resonances at certain sample orientations now allowed the assignment of specific quadrupolar tensor orientations within these sites for the larger quadrupolar coupling of the sites with $n = 1 \ldots 3$. The theory of the electronic structure including a model for lattice relaxation gives a physical interpretation of the ordering in this crystal lattice.

In Chapter 4 the semiconductor InGaP demonstrates very different properties. Perhaps one of the most important one is that the lattice dimensions of InP and GaP, do not match as well as AlAs and GaAs, which is causing stress in the InGaP lattice. While in AlGaAs the large arsenic quadrupolar distributions were mainly caused by the higher order shell `isotropic background’, in InGaP the distribution is mostly determined by inhomogeneous first shell contributions.

This chapter introduces a selection of quantum and classical physics concepts to the reader required to understand a part of the basic functionality of NMR. First, we briefly introduce the quantum concepts of nuclear spins, spin states, spin population and energy levels. A simplified interpretation of the NMR dynamics given with a vector model and the equations of motion. Furthermore, the spin echo sequence is described and applications of this sequence are presented. Finally, an overview of several possibilities to enhance the sensitivity of NMR is given and MRFM is introduced. In the MRFM section a short introduction to the other five MRFM Chapters is given.
1.3 Nuclear spin states

Each element of the periodic table has its own characteristic properties, such as mass, number of electrons, neutrons and protons, etc. An intrinsic quantum mechanical property of the nucleus is the spin. The values of the spin angular momentum $J$ of the nucleus are quantized. The allowed values are

\[ J = \hbar \sqrt{I(I + 1)} \]  

with $I$ the nuclear spin quantum number. The corresponding magnetic dipole moment can be calculated with

\[ \mu = \gamma \hbar I \]  

where $\gamma$ is the gyro magnetic ratio and $\hbar$ is the Planck constant divided by $2\pi$. If there is no external magnetic field, the orientation of the magnetic moment is random. For an ensemble of spins the distribution of the orientations is isotropic.

Let us now consider a single nucleus with a nuclear spin quantum number $I = 1/2$, for example, a proton. When this proton is placed in a static magnetic field $B_0$, by convention along $z$, two discrete quantum states with $m = \pm 1/2$ for the $z$-component of $I$ can be distinguished. The two quantum states (spin-up and spin-down) have oppositely directed angular momenta in the $z$-direction. This can be formulated with a quantum operator $\hat{I}_z$ acting on a quantum eigenstate $|\psi>$

\[ \hat{I}_z |\psi> = m |\psi> \]  

The $z$-component of the magnetic moment $\mu$ is different for each of the two states

\[ \mu_z = \gamma \hbar I_z \]  

Placed in a magnetic field, the nuclear spin precesses around the longitudinal, magnetic field $B_0$ (along $z$) with the Larmor frequency $\omega_0$ (see figure 1.1). The Zeeman Hamiltonian operator $\hat{H}$ for this spin system can be written as

\[ \hat{H} = -\mu_z \cdot \vec{B} = -\gamma \hbar I_z B_0 \]  

The eigenfunctions of $\hat{H}$ describe the possible states for the spin system[2]. The eigenvalues are the energies associated with the different eigenstates $|\psi> = |I, m>$. They can be written as

\[ \hat{H} |I, m> = E_m |I, m> \]  

Substituting the above two equations, the energy difference of the two Zeeman states is ($\Delta m = 1$)

\[ \Delta E = \gamma \Delta m \hbar B_0 = \hbar \omega_0 \]  

with $\omega_0 = \gamma B_0$. By irradiating at the Larmor frequency, transitions can be induced, which affects the populations of the energy levels. In general, we deal with macroscopic samples where there is an ensemble of spins. This means that for one milligram of sample there are $\sim 10^{16} \ldots 10^{20}$ nuclear
spins. The energy separation between the two states is relatively small and the energy from thermal collisions is sufficient to place many nuclei into higher energy spin states. The number of nuclei in each spin state can be described by the Boltzmann distribution. The Boltzmann equation expresses the relationship between temperature $T$ and energy $E$.

\[
\frac{N_{\text{upper}}}{N_{\text{lower}}} = \exp \frac{\Delta E}{k_B T}
\]

(1.8)

Where $N_{\text{upper}}$ and $N_{\text{lower}}$ represent the population of nuclei in upper and lower energy states. The Boltzmann distribution causes the lower energy eigen-state to be more populated than the higher energy eigen-state. The population difference at room temperature is very small (about 1 in $10^5$ spins, at a field of $\sim 10$ Tesla). This means that there is only a weak polarization present, that is responsible for pointing the majority of the nuclear spin angular momenta along the direction of the external magnetic field. Since every spin has a dipolar moment, this translates into the ensemble of spins having a macroscopic magnetization. In common NMR spectroscopy an coil can induce and pick up changes in this magnetization. Via this effect, the electrical signal of an NMR measurement describes the evaluation of the ensemble of spins in time.

In quantum physics, the changes in the population can be described with density operators (propagators) and matrices. The macroscopic magnetization is the observable of the system. The expectation value of the observable $z$-component of the magnetization depends on the sum of the contributions from each eigen-state, scaled by their populations. The ensemble average of the magnetic moment can be written as

\[
\langle \hat{\mu}_z \rangle = \gamma \hbar \langle \hat{I}_z \rangle
\]

(1.9)

and a quantitative value for the macroscopic magnetization $M_0$ in the equilibrium state can be derived (see [3])

\[
M_0 = |\langle \hat{\mu}_z \rangle| = \frac{n\gamma^2\hbar^2 I(I+1)B_0}{3k_B T} = \frac{C}{T} B_0
\]

(1.10)

where $C$ is the Curie constant and $n$ the total number of nuclear spins in the sample.
1.4. Equations of motion

Besides the quantum mechanical descriptions of energy levels, populations and spin states, the orientation of the macroscopic magnetization from an ensemble of spins from a practical point of view can be visualized in a classical vector representation. In a magnetic field $B_0$, the nuclear spins will tend to align themselves along this field. Not every spin has to be oriented along $B_0$ but the net magnetic moment is. In thermal equilibrium, the macroscopic magnetization will point along $B_0$.

The population of the spin levels can be manipulated by applying a weak transversal magnetic field $B_{1z}$ (~nT) at the Larmor frequency. A so called 90 degree RF pulse rotates the orientation of the net magnetization to the $xy$-plane. The magnetic resonance signal is measured in the laboratory (LAB) frame, but can be transformed to an on-resonance ($\omega_0$) rotating frame, where the spins signal oscillates much slower. The orientation and magnitude of the net magnetization can be described in this rotating frame with a vector $\vec{M}$. After the application of the RF pulse, $\vec{M}$ will relax to return to its equilibrium state $M_z$, with a time constant $T_1$ (longitudinal spin-lattice relaxation time). In the relaxation process of returning to equilibrium in the $z$-direction, the spins also lose coherence among each other in the transversal plane. This happens at the rate of the spin-spin relaxation time constant $T_2$. Figure 1.2 depicts these two relaxation processes.

The Bloch equations are a set of macroscopic equations that are used to calculate the nuclear magnetization as a function of time when relaxation times $T_1$ and $T_2$ are present

$$ \frac{\partial \vec{M}}{\partial t} = \gamma \vec{M}(t) \times B_{\text{eff}}^\omega $$

with $\vec{M}(t)$ the macroscopic magnetization as a function of time. The applied effective magnetic field $B_{\text{eff}}$ can be derived by considering a vector representation of the applied magnetic fields in the rotating frame. The resonance offset frequency with respect to the Larmor frequency is $\Omega = \omega - \omega_0$, 

![Figure 1.2:](image_url)
along the z-direction and the applied field strength along the x-direction is $B_{1x}$. The strength of the applied effective magnetic field is determined by the length of the two orthogonal vectors $B_{eff} = \sqrt{B_{1x}^2 + (\Omega/\gamma)^2}$. Including transversal spin-spin relaxation $T_2$ and longitudinal spin-lattice relaxation $T_1$, the equations of motion in the rotating frame, directly after the 90 degree pulse, are

$$
\begin{align*}
\frac{\partial M_x}{\partial t} &= \Omega M_y - \frac{M_x}{T_2} \\
\frac{\partial M_y}{\partial t} &= -\Omega M_x - \frac{M_y}{T_2} \\
\frac{\partial M_z}{\partial t} &= -\frac{M_z - M_{z0}}{T_1}
\end{align*}
$$

(1.12)

After the pulse, the two energy levels of the spin system are approximately equally populated. The energy levels will return to their original Boltzmann population through the spin-lattice relaxation process at the typical time constant $T_1$.

The time-signal or FID, that is measured by the spectrometer, consists of a real and an imaginary part. It contains the different contributions of the spin interactions, however, it is very difficult to visualize the interactions in the time domain. Therefore, a Fourier transformation is normally applied to transform the time domain signal to the frequency domain where the spectroscopic features can easily be distinguished. In the same way as the FID, the spectrum consists of a real part and an imaginary part. The real part of the spectrum is called the 'absorption' spectrum and the imaginary part 'dispersion'.

1.5 Nuclear spin interactions

In a static powder spectrum, each crystal orientation is responsible for a part of its, usually broad, spectrum. A single crystal, on the other hand, in theory has only a single crystal orientation, which should give very narrow lines, given that there are no distributions in the relevant nuclear interactions. Generally, liquid samples yield even sharper resonance peaks in NMR spectroscopy, provided they are homogeneous and diamagnetic. Due to rapid isotropic molecular tumbling, the dipolar interaction and chemical shift values are averaged. In general, when the liquid becomes more viscous and/or the molecule is larger, such as a protein, more broadening is expected.

In this section, the most relevant spin Hamiltonian operators that describe solid-state interactions in semiconductors are discussed. These interactions comprise the chemical shift anisotropy, the direct dipole-dipole interaction and the quadrupolar interaction.

1.5.1 Chemical shift

The electrons that surround a nucleus are not impasive in the magnetic field used in the NMR experiment, but react to it. The secondary field is generated by currents in the electron orbitals of the molecule induced by the external magnetic field $B_0$. The circulating molecular currents generate local magnetic fields. The nuclear spins experience the sum of the externally applied field and the induced fields generated by the electrons. The induced fields are in the order of $10^{-4}$ to $10^{-6}$ times $B_0$. However, it is enough to give rise to measurable shifts in the nuclear spin precession
1.5. NUCLEAR SPIN INTERACTIONS

![Image: A diagram showing nuclear spin interactions.]

**Figure 1.3:** (a) $^1$H ethanol spectrum showing three resonances with different chemical shift. From left to right the OH, CH$_2$ and CH$_3$ groups. (b) Solid-state powder spectrum of the Chemical Shift Anisotropy (CSA) for nuclei in a lattice with a non-axial symmetry.

frequencies. The magnitude of the chemical shift correlates with the electronegativity of neighboring groups. The chemical shift can be influenced by neighboring molecular units with a strong magnetic susceptibility, for example the ring-current shift in molecules with aromatic rings. The chemical shift from the NMR spectrum contains information of the local electronic environment. The chemical shift Hamiltonian can be written as [4, 2],

$$
\hat{H}_{cs} = \gamma \mathbf{I} \cdot \hat{\sigma} \cdot \vec{B}_0
$$

which describes the interaction between the nuclear spin $\mathbf{I}$ and the magnetic field $\vec{B}_0$ via the shielding tensor $\hat{\sigma}$.

Figure 1.3a displays the $^1$H ethanol spectrum. In ethanol (CH$_3$CH$_2$OH) there are three different environments for the hydrogen atoms: CH$_3$ - three hydrogen atoms in the same environment, CH$_2$ - two hydrogen atoms in the same environment and OH - One hydrogen atom in a unique environment. Therefore, there will be three discrete resonance peaks in the NMR ethanol spectrum. The rapid tumbling of molecules in a liquid averages any anisotropic chemical shift resulting in much sharper resonance peaks in comparison with solids.

For a solid-state sample in general, three types of symmetries in the lattice can influence the spectral fingerprint. First, there can be a non-axial symmetry for the nuclei in the lattice, where the shielding is different in all three dimensions. Figure 1.3b displays the spectrum for this type of anisotropy. Second, axial symmetry will also have a specific fingerprint in the spectrum. Here one site can identify the molecule perpendicular to $B_0$, while the other site identifies the molecule parallel to $B_0$. Finally, a spherical symmetry results in similar chemical shift shielding in all directions. In other words the chemical shift anisotropy is $\sim 0$. Note that in a powder spectrum the isotropic chemical shielding has the average value of $\sigma_{iso} = \frac{1}{3} (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$, where $\sigma_{ii}$ for $i = x,y,z$ are the diagonal elements of the chemical shift tensor.
1.5.2 Dipolar interaction

Since a nuclear spin has a magnetic moment, it generates a small magnetic field, which interacts with nearby spins. This is the dipolar interaction, see figure 1.4. The dipole-dipole coupling may be intra- or inter-molecular. The dipolar interaction can be described in terms of the homo- and hetero-nuclear dipolar Hamiltonians [2, 4]. In the first-order average Hamiltonian approximation, the dipolar Hamiltonian can be simplified by considering only the secular part (the part that commutes with the Zeeman Hamiltonian). Thus, the dipolar Hamiltonian for the homo- and hetero-nuclear interactions, \( \hat{H}_{II} \) respectively \( \hat{H}_{IS} \), can be written as

\[
\hat{H}_{II} = \sum_{jk} d_{jk} (3 \hat{I}_j z \hat{I}_k z - \hat{I}_j \cdot \hat{I}_k) \tag{1.14}
\]

\[
\hat{H}_{IS} = \sum_{jk} d_{jk} 2 \hat{I}_j z \hat{S}_k z \tag{1.15}
\]

where \( d_{jk} = \frac{b_{jk}}{2 \pi} (3 \cos^2 \theta - 1) \) the dipole-dipole coupling and \( \theta \) the angle between the vector joining the spins and the external magnetic field. The magnitude of the dipole-dipole coupling constant \( b_{jk} \) is

\[
b_{jk} = \frac{\mu_0 \gamma_j \gamma_k \hbar}{4\pi r_{jk}^3} \tag{1.16}
\]

The determination of the dipolar coupling is useful for structure elucidation, since it depends on known physical constants and it is proportional to \( r_{jk}^{-3} \) (\( r_{jk} \) is the nuclear distance between the \( I_j \) and \( I_k \) spins).

It is worthwhile to mention that dipolar couplings contain valuable information about the molecular structure, giving distance and angles between nuclear pairs. The angular dependency is an important feature. In liquid-state this contribution is averaged to zero due to the molecular tumbling, this gives access to highly resolved NMR lines.

1.5.3 Quadrupolar interaction

Around 74% of the NMR active nuclei have a spin quantum number \( 1 > 1/2 \) and are termed quadrupolar nuclei[2]. For such nuclei, the charge distribution is non-spherical. The surrounding electron clouds and the neighboring atoms generate an Electric Field Gradient (EFG) with which the nuclei interact via their nuclear quadrupole moment (see figure 1.5a). A Principle Axis Frame (PAF) is defined where the EFG tensor \( \hat{V} \) is purely diagonal. In this diagonalized form the following conventions
1.5. NUCLEAR SPIN INTERACTIONS

Figure 1.5: (a) 2D representation of a quadrupolar nucleus with a scalar quadrupole moment which interacts with the electric field gradient generated by the surrounding electron clouds and neighboring atoms. The ellipsoid shape and arrow represents the quadrupolar tensor orientation[4]. (b) The definition of the polar angles (φ and θ). They are needed for transforming interactions from the LAB frame with x,y,z coordinates to the PAF. In MAS φ = ωr · t and θ = 54.74°.

will be used (throughout this thesis)

\[\begin{align*}
eq_q & = \frac{V_{zz}}{V_{zz}} \\
\eta & = \frac{V_{xx} - V_{yy}}{V_{zz}} \\
C_q & = \frac{e^2 qQ}{\hbar} \\
\nu_q & = \frac{3C_q}{2I(2I-1)}
\end{align*}\]  

(1.17)

note that |V_{zz}| ≥ |V_{xx}| ≥ |V_{yy}| and the asymmetry parameter 0 ≤ η ≤ 1. This derivation uses the fact that the EFG tensor is traceless in any frame, i.e. V_{xx} + V_{yy} + V_{zz} = 0. e is the elementary charge, V_{zz} the largest gradient in the EFG tensor, C_q the quadrupole coupling constant, Q the scalar quadrupole moment of the nucleus and \nu_q the quadrupolar frequency. The general form of the quadrupolar Hamiltonian is

\[\hat{H}_Q = \frac{eQ}{2I(2I-1)\hbar} \hat{\mathbf{I}} \cdot \mathbf{V} \cdot \hat{\mathbf{I}}\]  

(1.18)

The quadrupolar Hamiltonian can also be written in terms of irreducible tensor operators [2, 5, 6] (see Section 3.5.3). The relevance of this decomposition is the particular transformation properties of the tensor under rotation, for instance, the scalar part remains invariant under rotations. The quadrupolar interaction is the largest interaction in NMR besides the Zeeman interaction. These two interactions can even become comparable in magnitude. Therefore, it is necessary to get the second order terms from perturbation theory. After discarding non-secular parts, the expression of
Figure 1.6: The simulated single crystal, static powder and MAS powder spectra of a quadrupolar nucleus with $I = 3/2$ (simulated with Simpson). $^{23}$Na spectra at $\nu_0 = 400$ MHz, $C_q = 250$ kHz, $\eta = 0$.

the first order quadrupolar Hamiltonian becomes,

$$\hat{H}^{(0)}_Q = \frac{\omega_Q(\theta, \phi)}{3} (3I_z^2 - I(I+1))$$  \hspace{1cm} (1.19)

$$\omega_Q(\theta, \phi) = \frac{\omega_Q^{PAF}}{2} (3\cos^2(\theta) - 1 + \eta_Q \sin^2(\theta) \cos(2\phi))$$  \hspace{1cm} (1.20)

$$\omega_Q^{PAF} = \frac{3\pi C_Q}{2I(2I-1)}$$  \hspace{1cm} (1.21)

in which the angles $(\phi, \theta)$ are spherical polar angles describing the orientation of the laboratory frame $z$-axis as defined by the direction of $B_0$, see Figure 1.5b. And the expression of the second order quadrupolar Hamiltonian is

$$\hat{H}^{(1)}_Q = \frac{\omega_Q^2}{\omega_0} \left[ \frac{1}{\sqrt{5}} A_{0,0} I_z [3I_z^2 - I(I+1)] \right]$$  \hspace{1cm} (1.22)

$$+ \frac{1}{2\sqrt{14}} A_{2,0} I_z [8I(I+1) - 12I_z^2 - 3]$$  \hspace{1cm} (1.23)

$$+ \frac{1}{2\sqrt{70}} A_{4,0} I_z [18I(I+1) - 34I_z^2 - 5]$$  \hspace{1cm} (1.24)

Note that the definition of $A_{n,0}$ is described in [2].

### 1.5.4 Quadrupolar anisotropy

Let us consider an application where a sample containing quadrupolar spins is placed inside a rotor and spinning under the so-called magic angle $\theta = 54.74^\circ$. Since the definitions of the quadrupolar interaction are defined in the Principle Axis Frame (PAF) (see equation 1.17), a transformation to the Laboratory (LAB) frame is needed. The transformation order and angular information can be described as,

$$PAF \rightarrow RAF \rightarrow LAB$$  \hspace{1cm} (1.25)

in which RAF the Rotary Axis Frame and $\omega_r$ the spinning speed. Here, for simplicity reasons, we assume that the sample in the rotor (RAF) is mounted exactly along the PAF. In this case, the first order quadrupolar contribution has an angular dependency $\frac{1}{2}(3\cos^2\theta - 1)$, i.e. the $P_2$ term of
1.5. **NUCLEAR SPIN INTERACTIONS**

![Graph showing NMR spectra](image)

**Figure 1.7:** The upper spectrum is the experimental $^{93}$Nb ($I = 9/2$) NMR spectra at $\nu_0 = 600$ MHz and $\omega_r = 15$ kHz MAS speed. The lower spectrum represents its best simulation.

the Legendre polynomial, see equation 1.21. Furthermore, this dependency is present as well in the chemical shift anisotropy, the direct dipolar interaction and the indirect J-coupling Hamiltonians. Mechanical fast rotation about the magic angle (Magic Angle Spinning or MAS) can efficiently remove these anisotropies leaving only the isotropic contributions. In solid-state NMR, experiments are routinely performed under MAS since it leads to line narrowing and spectral resolution. The second order contribution depends on the $P_4$ Legendre polynomial, which becomes zero at $\theta = 30.6^\circ$ and $70.1^\circ$. Therefore, this contribution will be the dominating term in a MAS NMR quadrupolar spectrum. For large $C_Q$, $\hat{H}_Q^{(1)}$ is insufficient to describe the spectrum accurately and $\hat{H}_Q^{(2)}$ must be taken into account.

For illustration purposes, figure 1.6 displays the single crystal, static powder and MAS powder spectra of an $I = 3/2$ nucleus with $C_q = 250$ kHz, $\eta = 0$ at $\nu_0 = 400$ MHz. The features of the quadrupolar interaction are clearly exhibited in the NMR spectra. Since the quadrupolar coupling is relatively low, the first order quadrupolar approximation is sufficient to describe the spectra. In the single crystal only one crystal and quadrupolar tensor orientation is present. In the spectrum $2I = 3$ lines are visible with a splitting of $\nu_Q = 125$ kHz. The three lines consist of a central transition (in the center) and two satellite transitions on the sides. In a powder all crystal orientations (equally divided on a sphere) are present. The static powder spectrum represents the quadrupolar signal from all crystal orientations. The contributions from all orientations result in a specific fingerprint, characteristic for these quadrupolar values. As described earlier, spinning around the magic angle, will remove the $P_2$ term of the Legendre polynomial leaving the isotropic contributions. In the MAS spectrum of figure 1.6 MAS sidebands appear at multiples of the spinning speed.

Figure 1.7 displays the solid-state $^{93}$Nb NMR MAS spectra of LiNbO$_3$ [7]. $^{93}$Nb has a large spin quantum number of $I = 9/2$ and a natural abundance of 100%. As explained earlier, due to the larger quadrupolar coupling constant ($C_Q \sim 23$ MHz, $\nu_Q = 958$ kHz), the line shape of the $^{93}$Nb MAS NMR spectrum needs to be described by incorporating also the second order quadrupolar perturbation terms. In this case, since $\eta \sim 0$ and $\theta = 54.7^\circ$ the contribution of $\hat{H}_Q^{(1)}$ is relatively small and the line shape is dominated by the second order quadrupolar interaction.
Figure 1.8: The spin echo concept of the pulse sequence \(90_\phi - \tau - 180_\phi - \tau - \) acquisition. (a) The vertical red arrow represents the net magnetization vector \(\vec{M}\) of a group of spins. A 90 degree pulse (along the x-axis, \(B_1\)) has been applied. (b) The magnetization is now flipped into the transversal plane. (c) Due to local magnetic field inhomogeneities that are spatially dependent (\(T_2^*\) effects), the net magnetization de-phases, some spins slow down due to lower local field strength (and begin to progressively trail behind) while some speed up due to higher field strength and start getting ahead. The different spin contributions broaden progressively and de-phase. (d) A 180 degree pulse is now applied in the x-direction. (e) The fast spin magnetic moments catch up and the slow moments drift back toward the average moment. (f) Complete refocusing has occurred and at this time, the echo is created and can be measured with all \(T_2^*\) effects removed.

1.6 Spin echoes

Echo phenomena are important features of coherent spectroscopy which have been observed and used in various fields from magnetic resonance to laser spectroscopy. Echoes were first detected in NMR by Erwin Hahn in 1950[8]. In nuclear magnetic resonance, a spin echo refers to the refocusing of precessing nuclear spin magnetization by a second on-resonance RF pulse. An extension of what was explained in the previous section can be made.

The NMR signal following an initial excitation pulse decays with time in the transversal plane due to both homogeneous spin-spin relaxation (\(T_2\)) and any other inhomogeneous effects (\(T_2^\prime\)) which cause different spins to precess at different rates. The experimental relaxation rate, extracted from the line width, is called \(1/T_2\). \((1/T_2 = 1/T_2 + 1/T_2^\prime\text{ (inhomogeneity)})\). Relaxation leads to spin de-coherence, resulting in an irreversible loss of magnetization. However, the dephasing due to inhomogeneous effects can be reversed by applying a 180 degree pulse that inverts the magnetization vector. If the inversion pulse is applied after a period \(\tau\) of de-phasing, the inhomogeneous evolution will re-phase to form an echo at time \(2\tau\) (see figure 1.8). The pulse sequence \(90_\phi_1 - \tau - 180_\phi_2 - \tau - \) acquisition is referred to as Hahn-echo sequence. The subscripts \(\theta_1\) and \(\theta_2\) refer to the phase of the RF pulses and \(\theta_3\) of the detection.

Hahn-echoes can be applied in many different situations. The most common reason to use Hahn
echoes is to get maximal signal intensity. The NMR intensity can become quite low in case broad spectral features have to be analyzed. In this case, the signal has already strongly decayed when the measurement starts. The Hahn-echo offers a means to circumvent the dead-time, i.e. receiver and acquisition delay. The dead-time is the time that the electronic probe circuit requires after the strong RF pulse is given and before the measurement of a relatively weak signal can proceed. Another reason to use echoes is that if a whole echo is recorded, the echo time signal is symmetric around its echo maximum. In a normal FID time signal, a time shift will lead to a phase twist in the frequency domain. However, in the whole echo, the Fourier transformed signal can be phased such that all spectral information ends up in the real spectrum and the imaginary part becomes zero.

The explanation is that the real part of the Fourier transformed signal can be reconstructed out of even functions, like the cosine function \( \text{Re}(F(\omega)) = \int_{-\infty}^{+\infty} f(t) \cos(\omega t) dt \), just like the whole echo time signal. This clever way of data acquisition and processing obviously has advantages (mostly for broad spectra). Another, well known application of the Hahn-echo is that by varying the delay time \( \tau \), the transversal relaxation can be monitored and the \( T_2 \) can be determined. A Hahn-echo can furthermore be used to refocus the magnetic field inhomogeneities. Any background NMR signal that comes from outside the detecting coil is not refocused by the second RF pulse (180 degree) and therefore is suppressed. Finally, by applying a phase-cycling on the 90 and 180 degree pulses, it is possible to select a certain coherence pathway, which can be useful, for instance, to record specific transitions of quadrupolar nuclei (quadrupolar nuclei are discussed in section 1.5.3).

1.7 CPMG

It is possible to suppress the effect of magnetic field inhomogeneities by using a pulse sequence with multiple echoes. This can only be done for samples with a long \( T_2 \) transversal relaxation time \( (T_2 >> \tau) \). The multi-echo sequence can improve the signal intensity by refocusing the effect of field inhomogeneities, which would otherwise cause spectral line broadening and thereby a reduction of the Signal-to-Noise Ratio (SNR). The pulse sequence is displayed in figure 1.9. It is an extension of the Hahn echo, by repeating the 180 degree pulse \( N \) times between the \( 2\tau \) intervals and is called CPMG[9]. The sequence took the name from its inventors Carr-Purcell-Meiboom-Gill (CPMG). The echo-train time signal is processed in the time domain and then Fourier transformed. This results in a spectrum with spikelets, where their intensities roughly follow the shape of the powder spectrum. By sacrificing spectral resolution, the effective SNR enhancement can amount to more than 50.
depending on the homogeneity of the $T_2$ of the sample. The sequence is particularly useful for solid-state samples exhibiting broad lines\cite{10}, where $T_2^* \ll T_2$ and low SNR. Typically, NMR spectra of nuclei with stronger quadrupolar interactions can become very broad. Although the integral of the original spectrum remains the same compared to a CPMG spectrum with a narrow line widths, in the original spectral the signal intensity is much lower. However, since the spectral line shape of these spectra is typically rather smooth, the spectral information can be acquired with a larger step size in the frequency domain. This can be done with the CPMG sequence. For quadrupolar spins this sequence is called QCPMG sequence. Note that this sequence was used in chapter 2.

1.8 2D NMR

When a 1D NMR spectrum gives insufficient information or is overlapping, a 2D NMR experiment can offer an alternative route to determine the desired NMR information. Generally, most NMR pulse sequences consist of a preparation, evolution, mixing and detection phase. A two-dimensional experiment is generated as a series of one-dimensional experiments, with a different preparation or evolution or mixing time in each successive experiment, with the duration of the detection period fixed.

The most popular 2D experiment for solids is homo-nuclear correlation spectroscopy (COSY). Here the time of the evolution phase changes in the second dimension. Diagonal peaks correspond to the peaks in the 1D spectrum, while cross peaks indicate couplings between pairs of nuclei. This 2D visualization is therefore well suited for structure determination of the molecule. Other 2D experiments are for example HETCOR, where two types of nuclei are correlated through spin-spin couplings, Heteronuclear Single Quantum Coherence (HSQC) correlates chemical shifts of directly bound nuclei, Heteronuclear Multiple Bond Correlation (HMBC) correlates chemical shifts of two types of nuclei separated from each other with two or more chemical bonds, Nuclear Overhauser effect spectroscopy (NOESY) where cross relaxation between nuclear spins during the mixing period is used to establish the correlations and Total correlation spectroscopy (TOCSY) which is similar to COSY, but the observed cross peaks are not only for nuclei which are directly coupled, but also between nuclei which are connected by a chain of couplings.

In this dissertation, the above mentioned techniques are not used. However, the following experiments are used and could be marked as being 2D: Multi Quantum Magic Angle Spinning (MQMAS), the frequency stepped QCPMG and nutation experiments. MQMAS is an echo experiment for quadrupolar nuclei in which a powder sample is mounted in a rotor and spinning under the magic angle. In this condition, a first pulse excites multi quantum coherence and a second pulse converts them to -1 quantum coherence. The detection is done on the central transition. In this manner the spectrum an separate the contributions from isotropic chemical shifts and isotropic quadrupolar shifts for different chemical sites\cite{11}, see for example Figure 4.4. The QCPMG sequence was introduce in Section 1.7. In case frequency stepping is used, a new spectrum exists for each resonance offset. A different frequency offset can have a serious effect on the excitation of a site and also on the phase of the spectrum, especially in case of a broad quadrupolar spectrum, see for example Figure 2.19. In nutation experiments, the pulse duration is incremented and the acquisition
1.9 NMR sensitivity enhancements

NMR is a great spectroscopic technique that can be applied to almost any sample with a nuclear spin $I \neq 0$. However, it has the major drawback of low sensitivity due to the earlier discussed low Boltzmann population differences at room temperature (see section 1.3). From equation 1.10 it follows that there are different ways to circumvent this issue, either by increasing the $B_0$ magnetic field, by having a larger sample volume, or by reducing the temperature. However, this is not always possible because low temperatures may affect or even destroy the sample, the natural abundance or gyromagnetic ratio of the nuclei is low, or because only few micrograms of sample are available. In these cases the sensitivity may simply be too low to get meaningful NMR spectra. An alternative approach to increase sensitivity is by means of polarization transfer. Since the signal enhancement depends on the energy splitting, strong enhancements can be obtained using polarization transfer from the electron to the nuclear spin energy levels. Polarization transfer between different nuclear energy levels can also give modest signal enhancements. However, these are much smaller than those achieved by involving electron spin levels. Furthermore, significant enhancements can be reached using different detection schemes. Various enhancement techniques are presented here.

Dynamic Nuclear Polarization (DNP) has its origins with the theoretical prediction of Overhauser[12] in 1953. The fundamental principle of DNP relies on the fact that if the conduction electron spins in a solid metal are saturated, the electron spin polarization can be transferred to the nuclear spins, resulting in a strong increase of the nuclear spin polarization. When electron spin polarization deviates from its thermal equilibrium value, polarization transfers between electrons and nuclei can occur spontaneously through electron-nuclear cross relaxation and/or spin-state mixing among electrons and nuclei. In particular, mechanisms for the microwave-driven DNP processes are categorized into the Overhauser effect (OE), the solid-effect (SE), the cross-effect (CE) and thermal-mixing (TM). Over the past fifty years, DNP has been used for polarization enhancements in diverse types of experiments, for example to obtain electron spin-lattice relaxation times[13] or to study molecular motion in solutions[14]. In a liquid, the polarization can be transferred via electrons contained in free radical molecules, added in minute amounts. The maximum enhancement with the Overhauser effect in the liquid state at room temperature is $\sim 0.5|\gamma_e|/|\gamma_I|$, which would be $\sim 330$ for protons and $\sim 1320$ for $^{13}\text{C}$ [15, 16]. The application of a weak RF field at the Larmor frequency on one of the spins for a sufficiently long time, has a strong effect on the longitudinal magnetization of the other, non-irradiated spins. This effect in some cases can even enhance the magnetization of the latter. The transfer of spin polarization from one spin population to the other occurs via cross-relaxation. This is called the steady state Nuclear Overhauser Effect (NOE). In modern liquid-state NMR, this is routinely applied in hetero-nuclear spin systems. The enhancement of the magnetization is $\sim 3$ for $^1\text{H}$ and $^{13}\text{C}$ [4].
A well known technique in NMR is Cross Polarization (CP). Efficient transfer occurs when the Hartmann-Hahn condition is reached. It means that the applied nutation frequencies \( \omega_1 = \omega_S \) of the two involved nuclei are matched. Then the polarization is transferred from the abundant nuclear spins of high gyromagnetic ratio to the rare nuclear spins of low gyromagnetic ratio, giving an enhancement factor of \(|\gamma_S|/|\gamma_I|\). This is about 4 for a polarization transfer from \(^1\text{H}\) to \(^{13}\text{C}\). Lin et al. showed that this scheme can be applied in MRFM [17].

In a static case, the Zeeman polarization can be stored in the dipolar reservoir by adiabatic down ramping of the amplitude of the RF field, afterwards the polarization can be recovered by up ramping the amplitude on the other nucleus [18] (see section 8.5). This technique is called Adiabatic De-magnetization in the Rotating Frame (ADRF) and Adiabatic Re-magnetization in the Rotating Frame (ARRF), reaching similar enhancements compared to CP.

Finally, for quadrupolar spins the populations of the satellite energy levels can be changed in order to enhance the population difference of the central transition. This can be done for instance using Double Frequency Sweeps (DFS)[3]. In general, the theoretical maximum enhancement factor is 2I.

Strong MR signal enhancements can be achieved using a more sensitive hardware detection geometry, \textit{i.e.} by improving the (optical, magnetic or mechanical) detection.

Optically Detected NMR (ODNMR) is more sensitive than conventional NMR because of the high energy of the detected light quanta compared to radio frequency[19]. Another possible advantage is the spatial selectivity by scanning the laser across the surface. In principle, two mechanisms of detection can be distinguished[20]. In the first mechanism the photons from a laser excite electrons in the material under study. The detection of the NMR signal proceeds indirectly via an optical signal which is modulated at the nuclear Larmor frequency. The applied oscillating optical signal generates an oscillating electron magnetization from the electrons in the sample. The electron spins interacts with nuclear spins of the sample through the hyperfine coupling [21]. This modulation can induce and measure NMR transitions in the presence of a static external \(B_0\) field, changing the forward/ reflected optical signal with respect to the applied optical signal. The induced change in the degree of circular polarization of the photo-luminescence signal can then be measured as a function of the NMR frequency [19]. The second mechanism of ODNMR occurs via time resolved Faraday Rotation (FR). The FR is a magneto-optical phenomenon which measures the interaction between light and a magnetic field in a medium. The rotation of the plane of polarization is proportional to the intensity of the component of the applied magnetic field in the direction of the light beam. In this manner, the spin precession frequency of the electrons in the conduction band can be measured with FR. As explained before, the nuclear spins interact with the electron spins through the hyperfine interaction. This interaction alters the precession frequency of the nuclear spins, which is used to measure the nuclear polarization. Unfortunately, since a magneto-optical medium is required, ODNMR is limited in its application to semiconductors. ODNMR was for example applied in bulk hetero-structures, for instance GaAs/AlGaAs, or GaAs quantum wells, where the nuclear polarization can be monitored through time-resolved optical measurements of electron spin dynamics. Poggio et al.[20] were capable of detecting a signal from \(\sim 10^{12}\) nuclear spins with FR.
1.10 Micro-imaging with NMR

Although NMR spectroscopy is a versatile tool which can be used to interpret complex molecular structures, besides this, the magnetic resonance signal can also be visualized in space. This technique, i.e. "NMR imaging" has become well known as Magnetic Resonance Imaging or MRI. In contrast to the strong, constant $B_0$ fields used in NMR, MRI requires strong gradient magnetic fields to achieve high spatial resolution imaging. A well known application of MRI is the visualization of a human body or brain. In MRI scanners in the hospital, the 3D spatial resolution is typically limited by a voxel size of about 1 mm$^3$ in 5 minutes [22]. Therefore, scanning the volume with a slightly higher resolution of $(100 \mu m)^3$ would take $\sim 10$ years to be completed with the same signal to noise ratio $(x10^6)$.

Clearly, for the study of small objects and high spatial resolution, this is not an option. To image these small volumes in a relatively short time frame, a novel technology is required. A major challenge for MR applications on micro volumes is to enhance the inherently low sensitivity. There are several ways to improve this, one possibility relies on the mechanical pickup of the NMR signal. In 1992, Sidles proposed a revolutionary technique called Magnetic Resonance Force Microscopy (MRFM) that allowed imaging of small samples[23].

Chapter 5 introduces the most important MRFM theory. Perhaps one of the most remarkable capabilities of MRFM is the imaging of micrometer volumes with chemical contrast[3]. In this aspect, MRI is now-a-days recognized as a powerful, 3D non-invasive microscopic technique. In the literature, different techniques are described that explain how to visualize micrometer interfaces of semi-conductors and biological samples with MR. New methodology in this field is of great importance. This requires new designs, new applications and different implementations.

In Chapter 6 we describe the designs of different MRFM prototype probes in which mechanical, optical, electrical and other issues are addressed. Specific attention was given to the interferometer optics and a novel strip line for MRFM. This strip line was designed in the clean room of MESA+ and was tested.

In Chapter 7 several MRFM applications are shown. Apart from these typical MRFM measurement results, one of the case studies concerns a semiconductor thin film of AlGaAs, that is
imaged on the basis of the magnetic resonance signal from each of the nuclei.

In Chapter 8 several novel schemes for spin manipulation in MRFM are shown and results are presented.

In Chapter 9 a feasibility study of real-space Fluor spin diffusion in KPF$_6$ is described.

In Magnetic Resonance Force Microscopy (MRFM), a sample is positioned in a strong ($10^3...10^6$ T/m) gradient magnetic field. Figure 1.10 displays the first MRFM design proposed by Sidles [23] in 1992. After this, many MRFM improvements were proposed by different designs and detection algorithms. Most MRFM designs contain a cantilever, i.e. a very sensitive spring which acts as mechanical displacement detector. In many different MRFM designs, the extremely small ($<$ nm) displacements are read out optically, either by fiber-optic interferometry or laser triangulation. Generally, a magnetic gradient source is required to generate the resonant regions per selected resonance frequency. The gradient source itself can simply be a piece of iron (using ferro-magnetism) placed in a strong static magnetic field $B_0$ (order of magnitude is several 100’s of MHz). A coil or wire can be used to generate a strong, perpendicular $B_1$ field along the x-axis (order of magnitude 100 kHz) in the sample. The sample can be either on top of the cantilever or on the surface with the magnetic gradient on the cantilever, which is often hanging directly above the sample[24].

Sidles’s first MRFM detection algorithm was amplitude detection during Fast Adiabatic Passages. In this type of MRFM detection algorithm, the RF frequency is swept from above resonance $+z$ to below resonance $-z$ periodically, with the cantilever eigen-frequency ($10^2...10^4$ kHz). The resonant frequency depends on the static $B_0$ field of the magnet, which is generally several 100’s of MHz. The sweep range is typically in the order of 1 MHz or smaller depending on the selected slice width. The static $B_0$, $B_1$ and the frequency offset generate an effective magnetization $B_{\text{eff}}$. The ensemble of nuclear magnetic dipole moments in the resonant slice of the sample (which is mounted on the cantilever here) will exert a periodic z-force on a cantilever, since the dipolar spins follow the induced, effective magnetization. In fact, if the sweep is adiabatic, the spins become ‘locked’ during the acquisition and invert periodically in longitudinal direction with every Fast Adiabatic Passage (see also section 5.8). Here, the modulated magnetization causes a periodic force or displacement, which can then be detected using for instance an optical interferometer. The optical signal is converted to an electronic signal with photo-diodes, is amplified and is detected phase-sensitive with respect to a reference frequency using a lock-in amplifier. The lock-in amplifier output can then be measured via an ADC card / port of a computer, is processed and graphically displayed. An overview of the experimental setup is given in Appendix D.

1.11 NMR enhancement mechanisms overview

An overview of the previously discussed MR signal enhancement techniques is given in table 1.1. The maximum enhancement factors are merely indicative of what to expect for the different techniques. The column with remarks displays the limitations and/or conditions. From this table it is clear
<table>
<thead>
<tr>
<th>Technique</th>
<th>Est. max. enhancement</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>MRFM</td>
<td>$\sim 10^2...10^{14}$</td>
<td>solid state, static measurement mechanical detection, low temperature</td>
</tr>
<tr>
<td>ODNMR</td>
<td>$\sim 10^5$</td>
<td>needs optical excitation/detection and semiconductor</td>
</tr>
<tr>
<td>CIDNP</td>
<td>$\sim 10^5$</td>
<td>needs optical excitation</td>
</tr>
<tr>
<td>DNP</td>
<td>$\sim 100$</td>
<td>needs microwave excitation</td>
</tr>
<tr>
<td>CP</td>
<td>$\sim 5$</td>
<td></td>
</tr>
<tr>
<td>NOE</td>
<td>$\sim 5$</td>
<td>for quadrupolar nuclei</td>
</tr>
<tr>
<td>DFS</td>
<td>$\sim 5$</td>
<td></td>
</tr>
</tbody>
</table>

**Table 1.1**: Overview of typical, estimated maximum enhancement factors of different techniques, with respect to conventional NMR detection at room temperature.

that MRFM is a very important technique since it has been proven to offer extremely high SNR enhancements for solid-state materials.
Chapter 2

A solid-state NMR and DFT Study of Compositional Modulations in \( \text{Al}_x\text{Ga}_{1-x}\text{As} \)

2.1 Abstract

We have conducted \( ^{75}\text{As} \) and \( ^{69}\text{Ga} \) Nuclear Magnetic Resonance (NMR) experiments to investigate order/disorder in \( \text{Al}_x\text{Ga}_{1-x}\text{As} \) lift-off films with \( x \sim 0.297 \) and 0.489. We were able to identify all possible \( \text{As}(\text{Al}_n\text{Ga}_{4-n}) \) sites with \( n = 0 \) to 4 coordinations in \( ^{75}\text{As} \) NMR spectra using spin-echo experiments at 18.8 Tesla. This was achieved by employing high rf field strengths using a small solenoid coil and an NMR probe specifically designed for this purpose. Spectral deconvolution, using an evolutionary algorithm, complements the absence of long-range order if a CuAu based order parameter is imposed. An unconstrained fit shows a deviation of the statistics imposed by this type of ordering. The occupational disorder in the Ga and Al positions is reflected in a distribution of the Electric Field Gradients (EFGs) experienced at the different arsenic sites. We established that this can be modeled by summing the effects of the first coordination sphere and a Czjzek type distribution resulting from the compositional variation in the Al/Ga sub lattice in the higher coordination spheres. \( ^{69}\text{Ga} \) 3QMAS and nutation data exclude the presence of highly symmetric sites and also show a distribution in the EFG. The experimentally obtained quadrupolar interactions are in good agreement calculations based on Density Functional Theory (DFT). Using additivity of EFG tensors arising from distant charge perturbations, we could use DFT to model the EFG distributions of the \( n = 0 \) to 4 sites, reproducing the Czjzek and extended Czjzek distributions that were found experi-
mentally. On the basis of these calculations we conclude that the $^{75}$As quadrupolar interaction is sensitive to compositional modulations up to the 7th coordination shell in these systems.

2.2 Introduction

Thin film semiconductors are of great importance for electronic and photonic devices. The development of new or improved devices relies on a detailed knowledge of the structural properties of the materials. In this respect compositional modulation and ordering play an important role. As was predicted by Zunger and coworkers [25] in the mid eighties, long-range order can occur in semiconductor alloys with size-mismatched constituents, despite the fact that the mixing enthalpy is positive. This can be explained by the fact that the statistical average over the many different local environments is positive, because some of these clusters are strained. Periodically repeating a three-dimensional geometric re-arrangement can minimize strain and leads to long-range order. These predictions were soon verified by experimental observations of ordering in semiconductors by Stringfellow and coworkers [26] and Gomyo and Suzuki [27].

For many III-V compounds the ordered phase has positive excess enthalpy, these structures can order metastably in bulk and can become stable in epitaxially grown films. Other crystallographic arrangements such as the CuPt structure do not possess enough geometrical degrees of freedom to permit all chemical bonds to attain their ideal length, and are therefore unstable. Nevertheless, ordering of alternating diagonal planes in the $<111>$ direction was found experimentally which was explained by assuming atomic dimerization at the surface, inducing CuPt ordering in the subsurface layers [28].

As there is hardly any size-mismatch in AlGaAs, long-range order has not been widely observed. Nevertheless, Krahmer et al. [29] reported evidence of a direct - indirect conduction band transition for $x = 0.4$ in Al$_x$Ga$_{1-x}$As by using reflectance anisotropy spectroscopy, indicating an increase in order. They report that doping, temperature and substrate orientation all affect the anisotropy of the lattice, but did not quantify this in terms of an order parameter. X-ray measurements from Kuan [30] et al. reported a low long-range order parameter $S < 0.5$ for Al$_{0.75}$Ga$_{0.25}$As grown by MOCVD, depending on growth conditions. More recent X-ray measurements by van Niftrik et al. [31] indicated a lower long-range ordering of $S \leq 0.05$ for Al$_{0.5}$Ga$_{0.5}$As and $S \leq 0.06$ for Al$_{0.25}$Ga$_{0.75}$As. Despite the prediction of almost no long-range ordering with X-ray, studies of the local interface for dilute AlGaAs with cross-sectional STM (XSTM) indicate the appearance of short strings. In 1994, an XSTM study by Smith et al. [32] confirmed that an interrupted growth process can create short period super lattices in AlGaAs. In 1996, Smith et al. [33] noticed a small deviation from random ordering in the Al-Al pair distributions at the interface of GaAs and Al$_{0.05}$Ga$_{0.95}$As. In 1999, Heinrich et al. [34] clearly observed strings of Al atoms in the GaAs matrix, up to five atoms in MOVPE grown Al$_{0.15}$Ga$_{0.85}$As along low indexed crystallographic directions.

In general, the composition of III-V semiconductors is difficult to describe since various structural features can exist (simultaneously) at different length scales. For instance, the presence of both ordered and disordered domains makes it hard to analyze these structures in detail. The degree of order will affect many physical and electronic properties such as electronic transport, mobility,
2.2. INTRODUCTION

thermodynamic stability and electro-optical properties. Many properties of AlGaAs are described in detail in the work of Adachi.[35] Considering the limited number of reports on long-range order in AlGaAs thin films as studied by diffraction techniques, whereas specific ordered structures are seen in a number of microscopic observations, it is interesting to study these materials with a complimentary method such as NMR. As NMR probes short-range order, the presence of locally occurring structures can be detected if present in sufficiently high concentrations. Since the NMR signal is composed out of contributions from the entire sample, the possibility that one is studying a specific anomaly is reduced. Long-range ordered structures will result in a specific signature which can be directly distinguished from a disordered structure.

NMR is a versatile technique that in principle can detect all nuclei which possess a spin through their interaction with an external magnetic field (the Zeeman interaction). A number of interactions make NMR useful as they give the spectra a specific appearance which can be related to local structure and dynamics of the material under study. In the present work two of these are important; the chemical shift and the quadrupolar interaction. The external magnetic field used in NMR induces local fields in molecules and materials that modify the resonance frequencies and makes different sites distinguishable, this is referred to as the chemical shift. For a \( I > 1/2 \) nucleus, the quadrupolar interaction arises from the presence of an electric field gradient (EFG), resulting from the local charge distribution around the site of a nucleus which interacts with the non-spherically symmetric charge distribution of that nucleus. Although NMR is an appealing technique that may form a bridge between diffraction studies and microscopic observations in the study of III-V semiconductors, there are a number of challenges that have to be addressed. Many nuclei encountered in III-V semiconductors are quadrupolar nuclei, possessing a large quadrupolar moment \( e \cdot Q \). The strength of the interaction expressed through the quadrupole coupling constant \( C_q = e^2 qQ / h \) can be very large, easily in the tens of MHz regime. Although this interaction can still be treated as perturbation of the Zeeman Hamiltonian, if sufficiently high external fields are applied, the quadrupolar interaction has, in general, to be treated as a second-order perturbation. To first-order the spectral features of the so-called satellite transitions are dispersed over a wide frequency range of the order of \( \nu_q = 3C_q/(2I(2I-1)) \) whereas the shape of the observed patterns reflects the asymmetry parameter \( \eta \) of the interaction. The central transition, \( \langle 1/2; -1/2 \rangle \) is not affected by the quadrupolar interaction in first order but the second-order features are dispersed over a frequency range of the order of \( \nu_q^2 / \nu_0 \), where the shape is again characteristic for the asymmetry of the EFG tensor. Even at high external fields this second-order interaction can result in MHz bandwidths for nuclei such as \(^75\)As. To excite such a bandwidth efficiently, sufficiently large rf field strengths are needed. In relation to this one has to realize that the behavior of the spin system in the rotating frame during rf-irradiation depends on the ratio of the quadrupolar frequency and the rf field strength.[36, 37] Therefore, the effective excitation of the spin systems has to be modeled accurately, especially when quantitative results of different spin systems with widely differing quadrupolar parameters are needed. Additionally, with such different sites present spectral overlap will often occur, demanding a robust approach to spectral deconvolution. Finally, to interpret NMR spectra in relation to structures, a first principle approach such as DFT is desirable.

In the present contribution we address all of the issues described above. Using small rf-coils it is possible to generate appropriate rf-fields to excite a broad bandwidth. These coils also help in
overcoming the sensitivity problems related to the study of thin film materials leading to very low quantities of sample material. Here we compare spin-echo experiments and frequency-stepped Quadrupolar Carr-Purcell-Meiboom-Gill (QCPMG) experiments to obtain static $^{75}$As spectra of two AlGaAs films with different composition. Spectral deconvolution and quantification of the spectra is addressed with a dedicated program based on an evolutionary algorithm. $^{69}$Ga 3QMAS and mutation NMR spectra have been obtained to gain complementary information about the local symmetry of the different lattice sites. Although this work focuses on AlGaAs thin film materials, the approach presented can be applied for the investigation of compositional modulations in most III-V semiconductors and materials with related variations in the occupancy of different lattice positions, sometimes called substitutional disorder.

Furthermore, we develop a modeling approach to accurately describe the EFG distributions of various kinds of sites. To this end we extended the first-principles DFT code of VASP (Vienna Ab initio Simulation Program), to calculate EFGs and build a model wherein we can quickly calculate the EFGs for several millions of configurations based on just one DFT calculation. This model is used to estimate the sensitivity of EFGs to variations in the order parameter. It has a wider scope, as it in principle provides the capability to quickly obtain electronic density distributions for any structural model for any “random” alloy with fixed sub-lattices.

2.3 Studying (dis-)order with NMR

Based on theory used to analyze diffraction data, an order parameter $S$ can be defined to quantify the degree of long-range order related to the fractional occupancy of lattice sites by their preferred atom. $S = 0$ represents a completely random structure and $S = 1$ corresponds to a completely ordered lattice:

$$ S = |r_A + r_B - 1|, $$

where $r_A$ and $r_B$ are the fractions of A and B lattice sites that are occupied by their preferred atom. For binary systems, as considered here, this means that $1 - r_A$ constitutes the fraction of A lattice sites occupied by B atoms and $1 - r_B$ the fraction of B sites occupied by A atoms. In case of random occupation of the lattice sites, i.e. the absence of ordering, $r_A = x$ and $r_B = 1 - x$. For (partially) ordered structures the fractional occupancy of the A and B sites by their preferred atoms can be re-written as:

$$ r_A = x + S/2 $$

$$ r_B = (1 - x) + S/2 $$

Using this definition we should realize that the order parameter $S$ can reach a value of $2x$ at most. A perfectly ordered structure can only be achieved for $x = 0.5$. $S$ can be scaled, however, so that the maximum possible order for any given composition $x$ gives an order parameter $S = 1$.

The presence of (dis-)order in a structure is in most cases manifested in quantifiable NMR parameters. Different structural environments in a material can be distinguished based on the NMR interactions which are influenced by the different coordinating atoms. For example, Tycko et al. distinguished five $^{31}$P sites in the $^{31}$P MAS NMR spectrum of GaInP. These five resonances were
assigned to the different phosphorus nearest neighbors coordinations \( \text{P[In}_{4-n}\text{Ga}_n] \) with \( n = 0-4 \). The sites are resolved in this spectrum due to their different isotropic chemical shifts. The presence of order in the sample is reflected in the statistics of the occurrence of the various coordinations \([43, 42]\). The probabilities \( p_n \) for the occupations of the \( \text{C[A}_{n}\text{B}_{4-n}] \) sites are

\[
\begin{align*}
p_0 &= p_{C[B_4]} \\
p_1 &= p_{C[A_1 B_3]} \\
p_2 &= p_{C[A_2 B_2]} \\
p_3 &= p_{C[A_3 B_1]} \\
p_4 &= p_{C[A_4]} 
\end{align*}
\] (2.4)

Here, two types of ordering are considered for \( \text{A}_x\text{B}_{1-x}\text{C} \) type materials, see Fig. 2.1. \( \text{CuPt} \) ordering, with diagonal planes, stacked in the \( <111> \) direction or a \( \text{CuAu} \), with alternating planes in \( <001> \). For each configuration, we can quantify the probability of their occurrence. The 16 possible atomic configurations in the first shell contribute each with a different probability:

\[
\begin{align*}
p_{0\text{CuPt}} &= \frac{1}{2} r_B (1 - r_A)^3 + \frac{1}{2} (1 - r_A) r_B^3 \\
p_{1\text{CuPt}} &= \frac{1}{2} (1 - r_B) (1 - r_A)^3 + \frac{1}{2} r_A r_B^3 + \\
 & \quad + \frac{3}{2} r_A r_B (1 - r_A)^2 + \frac{3}{2} (1 - r_B) (1 - r_A) r_B^2 \\
p_{2\text{CuPt}} &= \frac{3}{2} (1 - r_B) r_A (1 - r_A)^2 + \frac{3}{2} r_A (1 - r_B) r_B^2 + \\
 & \quad + \frac{3}{2} (1 - r_B)^2 r_B (1 - r_A) + \frac{3}{2} r_A^2 (1 - r_A) r_B \\
p_{3\text{CuPt}} &= \frac{1}{2} r_A^3 r_B + \frac{1}{2} (1 - r_B)^3 (1 - r_A) + \\
 & \quad + \frac{3}{2} r_A^2 (1 - r_B) (1 - r_A) + \frac{3}{2} (1 - r_B)^2 r_A r_B \\
p_{4\text{CuPt}} &= \frac{1}{2} (1 - r_B) r_A^3 + \frac{1}{2} r_A (1 - r_B)^3 
\end{align*}
\] (2.5)
\[ p_0^{CuAu} = (1 - r_A)^2 r_B^2 \]
\[ p_1^{CuAu} = 2r_A(1 - r_A)r_B^2 + 2(1 - r_B)(1 - r_A)^2 r_B \]
\[ p_2^{CuAu} = r_A^2 r_B^2 + (1 - r_B)^2 (1 - r_A)^2 + 4r_A(1 - r_B)r_B(1 - r_A) \]
\[ p_3^{CuAu} = 2r_A^2 (1 - r_B)r_B + 2r_A(1 - r_B)^2 (1 - r_A) \]
\[ p_4^{CuAu} = (1 - r_B)^2 r_A^2 \] (2.6)

As the probabilities correspond to the integrated peak intensities of the different sites, one can determine the long-range order parameter by drawing the experimental peak intensities in a plot of calculated intensities versus order parameter \( S \). Using the relative \(^{31}\text{P}\) peak intensities Tycko et al.\[43\] were able to set an upper limit of \( S < 0.6 \) for the CuPt type ordering in InGaP. Degen et al.\[42\] observed the \(^{75}\text{As}\) resonances of the locally symmetric \( \text{As}[\text{Al}_4] \) and \( \text{As}[\text{Ga}_4] \) coordinations in static single-pulse excitation experiments on powdered AlGaAs films. They were able to set an upper limit of \( S < 0.2 \) and \( S < 0.4 \) for CuAu and CuPt ordering respectively. Although spin-echo experiments hinted at the presence of the other \(^{75}\text{As}\) coordinations, these proved to be too broad to be efficiently excited and resolved in the spectrum.

Finding low values for the long range order parameter \( S \) indicates that the atomic distribution of A and B atoms becomes more or less random over their lattice positions. It may well be, however, that there is still a preference for local ordering of Al and Ga in the sample, e.g., when A atoms prefer B atoms in their vicinity and vice versa. Alternatively, atoms can show a tendency to be close neighbors which is referred to as clustering. Short-range ordering and clustering is very difficult to detect with diffraction techniques as they cause only very weak diffuse scattering. In NMR the statistics of the different coordinations will be modulated by either short range order or clustering, which should be expressed in increased numbers for \( p_0 \) or \( p_4 \). The exact effect and size of the variations will depend on the scale and abundance of the locally ordered structures and may be difficult to interpret depending on the accuracy with which the spectral line intensities can be determined.

Besides modulating the intensities of the various C[\( \text{A}_n\text{B}_{4-n} \)] resonances in the spectra it should be realized, however, that the distribution of A and B atoms over the lattice also affects the NMR parameters such as the chemical shift and the quadrupolar interaction parameters \( \nu_q \) and \( \eta \) of these sites. Especially for the quadrupolar interaction it is important to consider that the interaction is not fully determined locally. Although the electric field gradient tensor is dominated by the first shell bonds, further coordination shells still have a distinct influence. This is witnessed by the fact that the symmetric first shell As coordinations, \( \text{As}[\text{Al}_4] \) and \( \text{As}[\text{Ga}_4] \), observed by Degen et al.\[42\] in AlGaAs, show non-zero quadrupolar interactions with quadrupolar coupling constants of 800 and 600 kHz respectively.

Structural disorder leads to distributions in chemical shift and quadrupolar interactions, which affect the measured line shapes in a characteristic way. Therefore, a detailed study of the line shapes in disordered solids can be interpreted in terms of structural variations in these materials if one can extract the probability density function for the quadrupolar interaction parameters from the spectra and compute the EFG tensors for a given structure, e.g., based on first principles DFT
based calculations.

Extraction of the probability density function from NMR spectra of randomly oriented powder samples is not trivial as the distribution in quadrupolar NMR parameters is convoluted with the powder averaging over all possible tensor orientations in the ensemble. In the NMR literature several approaches to model the probability density function(s) for the quadrupolar interaction parameters can be found. The most basic approach is to assume Gaussian distributions in \( C_q \) and \( \eta \). Although such distributions are not physically justified they regularly do produce line shapes similar to the experimental ones and can therefore be used in spectral deconvolutions in order to properly quantify the relative line intensities. One should be careful with interpreting these results in terms of structural disorder, however, especially where the asymmetry parameter \( \eta \) is concerned. First of all, the structural parameters are not additively described by quadrupolar parameters and are therefore not expected to be normally distributed and moreover \( \nu_q \) and \( \eta \) are coupled as they both depend on the local electronic coordination around a nucleus. Jäger et al.\cite{44} and Meinhold et al.\cite{45} have improved on this basic model by assuming normal distributions in the eigenvalues of the EFG tensor and applying constraints to warrant the tracelessness of this tensor. Again good line shapes can be obtained but this approach is still not satisfactory as \( C_q \) and \( \eta \) are treated independently, needing a starting value for \( \eta \). Moreover, the distribution is generated numerically lacking an analytical description.

A physically more sound model for describing the distribution of electric field gradients in amorphous solids has been developed by Czjzek et al.\cite{46} They proposed a joint probability density function

\[
P(V_{zz}, \eta) = A \cdot \exp \left( -\frac{V_{zz}^2 (1 + \eta^2/3)}{2 \sigma^2} \right),
\]

\[
A = \frac{V_{zz}^{d-1} \cdot \eta (1 - \eta^2/9)}{\sqrt{2 \pi \sigma^d}},
\]

in which the average quadrupolar coupling constant depends on \( \sigma \) and \( d \), see table 2.1. In this work, we show that for a randomly ordered lattice, the quadrupolar distributions caused by a random occupancy of the A and B sites over the lattice can be described by a Czjzek distribution with \( d = 5 \) for the symmetric C[A\(_4\)] and C[B\(_4\)] sites. These distributions are isotropic and rotation invariant. Eq. 2.7 is derived from the fact that the real terms \( U_m(m = 0-4) \) (defined in references \cite{46, 47}) of the EFG tensor are independently, normally distributed variables for amorphous solids with random ionic coordinations. The five independent spherical tensor elements \( V_{i,k} \) of the EFG tensor are linear combinations of these \( U_m \). A similar approach was introduced by Stöckmann \cite{48} describing the effect of randomly distributed defects in cubic crystals.

As was outlined by Massiot and coworkers\cite{49}, the Czjzek distribution can only be used if the number of structural elements contributing to the EFG is sufficiently large, meaning that for a given coordination shell the coordination number should be large. This will in general not be the case for the first coordination shell. Therefore the Czjzek distribution can in principle only be used if the first coordination sphere hardly contributes to the EFG as is the case for the symmetric As[Al\(_4\)] and As[Ga\(_4\)] sites in AlGaAs or the octahedrally and tetrahedrally coordinated aluminium sites discussed by Massiot et al.\cite{49}. Clearly, the first coordination sphere dominates the EFG for the asymmetric As[Al\(_n\)Ga\(_{4-n}\)] sites with \( n = 1, 2, 3 \) in AlGaAs. To deal with this situation an
Table 2.1: The ratio of the average \( < V_{zz} > \) to the \( \sigma \) in a Czjzek distribution as a function of the power factor \( d \) obtained by integrating Eq. 2.7 over all \( \eta \) for a given \( \sigma \).

<table>
<thead>
<tr>
<th>( d )</th>
<th>( &lt; V_{zz} &gt; / \sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.74</td>
</tr>
<tr>
<td>2</td>
<td>1.17</td>
</tr>
<tr>
<td>3</td>
<td>1.49</td>
</tr>
<tr>
<td>4</td>
<td>1.76</td>
</tr>
<tr>
<td>5</td>
<td>2.00</td>
</tr>
</tbody>
</table>

An extension of the Czjzek approach is needed, considering the case of an EFG contribution of a well-defined local coordination of a given atomic species and adding to that the effect of disorder of more remote atomic shells and possible other random contributions to the total EFG. Due to the good lattice matching of the AlGaAs lattice, we neglect any stress in the lattice and propose to use additivity for the local and remote contributions to these EFGs. This is implemented numerically by adding the (fixed) contribution of the first coordination shell to the Czjzek distribution resulting from (random) occupancy of Al and Ga lattice sites in the further coordination shells. First, the principal EFG tensor values are generated from the Czjzek distribution using \( V_{xx} = -V_{zz}(\eta + 1)/2 \) and \( V_{yy} = V_{zz}(\eta - 1)/2 \). The resulting tensor \( V \) is then rotated over a set of Euler angles using \( V_{\text{rot}} = R(\alpha, \beta, \gamma) \cdot V \cdot R(\alpha, \beta, \gamma)^T \), with \( R^T \) the transposed rotation matrix. The relative orientation is randomized by taking all possible orientations into account. The first shell EFG is added to this tensor after which it is diagonalized and sorted using \( V_{zz} \geq V_{xx} \geq V_{yy} \). The final distribution is generated by integration over all possible angles on a sphere ensuring the isotropic character of the distribution. The resulting \( V_{zz} \) and \( \eta \) values are placed on a new grid with the weights of the original Czjzek distribution. For Al\(_2\)Ga\(_2\), the first shell tensor \( V(0) \) is defined by a single scalar value \( V^\eta_1 \) and \( \eta(0) = 1 \)

\[
V = \begin{bmatrix}
-V^\eta_1 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & V^\eta_1
\end{bmatrix}
\] (2.8)

The first shell tensor of a Al\(_2\)Ga\(_3\) / Al\(_3\)Ga\(_1\) site is defined by \( V^\eta_0 \) and \( \eta(0) = 0 \)

\[
V = \begin{bmatrix}
-V^\eta_0/2 & 0 & 0 \\
0 & -V^\eta_0/2 & 0 \\
0 & 0 & V^\eta_0
\end{bmatrix}
\] (2.9)

The "extended Czjzek" distribution generated in this way coincides with the extended Gaussian Isotropic Model (GIM) introduced by Le Caër and Brand[47]. These authors give an in-depth and general discussion of models for the distributions of electric field gradients in disordered solids. Their extended Gaussian Isotropic Model (GIM) considers the case of an EFG tensor \( V_0 \) added to a random tensor background contribution \( \tilde{V}_{\text{G}1} \) with a ratio \( y \), \( \tilde{V} = (1-y) \cdot V_0 + y \cdot \tilde{V}_{\text{G}1} \). Here we assign \( y = 0.5 \), since there is an equal contribution of the EFG tensor from the higher coordination spheres and the first coordination shell. Since a normalization is missing, it is more convenient to consider \( \tilde{V} = V_0 + \tilde{V}_{\text{G}1} \). Le Caër and Brand describe the quadrupolar distribution by an exponential expression of three terms, integrated over a sphere, see [47], using the Euler angles \( \alpha, \beta, \gamma \). This
equation is slightly modified here into Eq. 2.10. The nominator of the exponent consists of a mix term \( \tilde{U} \cdot \tilde{U}'(0) \), an offset term which is constant \( V_{zz}(0)^2 \cdot (1 + \eta(0)^2/3) \) and merely scales the intensities and a Czjzek term \( V_{zz}^2 \cdot (1 + \eta^2/3) \). The “ordered” first shell tensor has magnitude \( V_{zz}(0) \) and an asymmetry parameter \( \eta(0) \). In comparison with \( \eta(0) = 0 \), there are two additional cross-terms in \( \tilde{U} \cdot \tilde{U}'(0) \), when \( \eta(0) = 1 \). Even though the offset term is constant, as the ratio \( V_{zz}/\sigma \) can become large, all exponential terms need to be placed inside the integral and cannot be placed in front, since individually the exponential terms can become extremely large > 10^{700} in case of a strong first shell tensor \( V_{zz}(0) > 40 \times 10^{20} \text{ V/m}^2 \).

\[
f(V_{zz}, \eta) \propto A \cdot \int \exp \left( \frac{\tilde{U} \cdot \tilde{U}'(0)}{2\sigma^2} \right) \frac{V_{zz}(0)^2 \cdot (1 + \eta(0)^2/3) - V_{zz}^2 \cdot (1 + \eta^2/3)}{2\sigma^2} d\omega \sin(\beta) d\beta d\gamma \]

\[
\tilde{U} \cdot \tilde{U}'(0) = 2 \cdot V_{zz} \cdot \left( V_{zz}(0) a_{11} + \frac{\eta(0) V_{zz}(0) a_{15}}{\sqrt{3}} \right) + \\
2 \cdot \eta V_{zz} \cdot \left( V_{zz}(0) a_{51} + \frac{\eta(0) V_{zz}(0) a_{55}}{\sqrt{3}} \right),
\]

(2.10)

with \( a_{ij}(\alpha, \beta, \gamma) \) as defined in ref. [47] and \( A \) as in Eq. 2.7. For \( \eta(0) = 0 \) this equation can be written into a modified Bessel function form (see Eq. 61 in ref. [47]). Practically, the \( (V_{zz}, \eta) \) distribution for \( \eta(0) = 0 \) showed good overlap with the previous equation in a simplified, approximated form without integral

\[
f(V_{zz}, \eta) \sim A \cdot \exp \left( \frac{V_{zz} \cdot V_{zz}(0)}{2\sigma^2} \right) \\
\frac{-V_{zz}(0)^2 \cdot (1 + \eta(0)^2/3) - V_{zz}^2 \cdot (1 + \eta^2/3)}{2\sigma^2}
\]

(2.11)

allowing a much faster calculation. The only difference with the extended Czjzek distribution that was introduced previously, is the scaling of the tensor terms and the extra \( y \) parameter. Although Le Caër and Brand [47] use \( y \) as a parameter for local ordering (crystalline, mixed or random domains), we consider this effect simply by adjusting the magnitude of the first shell tensor \( V(0) \), omitting the need for an extra variable in this approach. Substituting \( V(0) = 0 \) corresponds to the original Czjzek distribution.

A final important step for interpreting distributions in quadrupolar NMR parameters is being able to predict the quadrupolar parameters on the basis of a given structural model. The calculation of EFGs using Density Functional theory (DFT) has been implemented in the Full Potential Linearised Augmented Plane Wave (FLAPW) method by Herzeg et al. [50] and in the PAW (Projector Augmented Wave) method by Petrilli et al. [51]. Following the latter we implemented the EFG calculation in the first-principles electronic structure program VASP (Vienna Ab initio Simulation Package) [52, 53, 54, 55]. An additional challenge in this context is to appropriately model the effects of the structural variations present in the material. In case of AlGaAs, however, the effects of
local charge (re)distributions arising from single lattice modifications are additive, so that various disordered configurations can be modeled with relatively low computational cost.

2.4 Experimental

2.4.1 Sample Preparation

The AlGaAs samples were grown by Metal Organic Vapor Phase Epitaxy. Undoped 2 inch GaAs wafers with crystal orientation $<100>$, 15 degrees off towards $<111>$ were used as substrates. A typical sample consisted of a 15 nm Si-doped AlAs buffer and a 5 $\mu$m undoped Al$_x$Ga$_{1-x}$As layer. A growth series with nominal aluminum fractions of $x = 0$, 0.297 was produced. A sample with $x = 0.489$ was grown on a substrate 2 degrees off towards $<110>$. An epitaxial lift-off process [36] was applied to separate the Al$_x$Ga$_{1-x}$As layer from the substrate by selectively etching the intermediate Si-doped AlAs layer with a hydrogen fluoride solution. The Al$_x$Ga$_{1-x}$As thin films ($\approx$ mg quantities) were crushed into a powder with a typical grain size of a few micrometers and subsequently transferred to plastic sample holders for NMR measurements. The sample holders were made of PolyEtherEtherKeton (PEEK).

2.4.2 NMR Experiments

A home-built, static XH probe operating at 137 MHz for arsenic (18.8T) was designed for achieving high $rf$ fields. The coil was a 5-turn solenoid with a 1.2 mm internal diameter, made of a silver-plated, 220 $\mu$m diameter wire. The sample space was confined to a length of 2 mm and a diameter of 0.6 mm. The Q factor of the probe was determined to be $\approx 38$. Two Allen-Bradley 1 k$\Omega$ high power resistors were put parallel to the tuning capacitor to reduce the Q factor to $\approx 20$ to allow frequency-stepped experiments without retuning the probe. The $rf$-field strength was determined by obtaining $^{75}$As nutation spectra from a sample of GaAs. In this sample As occupies a cubically symmetric lattice and therefore the signal mutates with frequency $\nu_{rf}$. $rf$ field strength up to 800 kHz were achieved using approximately 800 Watts of power. In the QCPMG and Hahn-echo pulse experiments very short pulses are used so one has to take into account that the maximum voltage is never reached due to the pulse rise time depending on the Q factor of the probe (see supplementary material). Therefore actual $rf$ fields amounted to 390 kHz and 625 kHz in the QCPMG and Hahn-echo experiment respectively.

I. $^{75}$As QCPMG: A well-established experiment for acquiring very wide-line spectra with high sensitivity is the frequency-stepped QCPMG experiment.[10, 39, 40, 9] For such an experiment it is useful to reduce the probes’ Q factor (here to 20). The flat response of the probe minimizes the phase variations as a function of frequency. This is advantageous since the probe does not need to be re-tuned and the intensity loss at large frequency offsets is almost negligible. 24 respectively 22 experiments were performed at 18.8T using a Varian InfinityPlus console. The frequency step size was 125 kHz covering a spectral width of 3 MHz for Al$_{0.297}$Ga$_{0.703}$As and Al$_{0.489}$Ga$_{0.511}$As. The $x \approx 0.297$ spectrum was recorded with 10,000 scans and the $x \approx 0.489$ with 5,400 scans.
at each frequency step. Because $T_2$ is long, the number of echoes acquired (242) was limited by experimental limitations (121,000 data points in 30 ms). The 90° and 180° pulse times were 0.32 µs and 0.64 µs respectively. A repetition delay of 1 second was used, acquiring a spectral width of 4 MHz. Each echo acquisition time was 125 µs with 7.5 µs experimental delay before and after the 180° pulse of each echo. The individual 500 point whole-echoes were $T_2$ weighted before co-adding, and subsequently swapped around the echo maximum and Fourier transformed. A more detailed description of acquisition and processing of the QCPMG data is given in the supplementary material.

II. $^{75}$As Hahn-echo: Hahn-Echo ($\frac{\pi}{2},-x,-\tau_1,-\tau_2,-ACQ^2,-x$) experiments were obtained at 18.8 T, corresponding to a $^{75}$As frequency of 136.93 MHz, using a Varian InfinityPlus Console. A recycle delay of 1 second was employed. Whole echoes were recorded which were processed by swapping the data around the echo maximum followed by apodization (exponential) and zero-filling to 8192 points before Fourier transformation. The spectral width was 5 MHz. The $x \approx 0.297$ Hahn-echo spectrum was acquired with 75,000 scans and echo times of $\tau_1 = 200$ µs, $\tau_2 = 75$ µs and 25 µs delay from the acquisition and receiver delay. The 90° and the 180° pulse times were 0.2 µs respectively 0.4 µs. 166,000 scans were averaged in the $x \approx 0.489$ Hahn-echo data with $\tau_1 = 175$ µs, $\tau_2 = 5$ µs and 20 µs delay from the acquisition and receiver delay.

III. $^{69}$Ga Nutation and 3QMAS: A series of $^{69}$Ga static nutation spectra using different rf-field strengths were obtained for $\text{Al}_{0.297}\text{Ga}_{0.703}\text{As}$ at 14.1 T on a Chemagnetics Infinity 600 MHz spectrometer. The same probe was used for these experiments, tuned to 143.99 MHz with a Q factor of $\sim 50$. A $x$-filtered $^{69}$Ga 3QMAS spectrum, using hyper-complex States TPPI[57] was recorded at 9.4 T, 96.013087 MHz, on a Chemagnetics Infinity 400 MHz spectrometer. Here a spinning speed of 15 kHz was employed, using a Chemagnetics 2.5 mm HX probe.

IV. Spin-lattice relaxation times: To ensure quantitative evaluations of the spectra, spin-lattice relaxation times were determined for $\text{Al}_{0.297}\text{Ga}_{0.703}\text{As}$ using saturation recovery experiments, as summarized in table 2.2. The values for this $x \approx 0.297$ composition do not differ strongly from the values determined earlier [42] for a sample with composition $\text{Al}_{0.498}\text{Ga}_{0.511}\text{As}$, indicating no significant changes in relaxation mechanism for different compositions. The $T_1$ of $^{75}$As in bulk GaAs was $0.33 \pm 0.05$ seconds.

2.4.3 Spectral deconvolution

An important objective of this study is to characterize the $^{75}$As coordinations in $\text{Al}_{x}\text{Ga}_{1-x}\text{As}$ and determine their relative intensities. The analysis can become complex due to the presence of several overlapping resonances with a distribution in NMR interaction parameters. Here we resort to fitting

<table>
<thead>
<tr>
<th></th>
<th>$\text{Al}<em>{0.297}\text{Ga}</em>{0.703}\text{As}$</th>
<th>$\text{Al}<em>{0.489}\text{Ga}</em>{0.511}\text{As}$[42]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{69}$Ga</td>
<td>-</td>
<td>$0.77 \pm 0.04$</td>
</tr>
<tr>
<td>$^{71}$Ga</td>
<td>$0.11 \pm 0.04$</td>
<td>$0.15 \pm 0.08$</td>
</tr>
<tr>
<td>$^{27}$Al</td>
<td>$18 \pm 1$</td>
<td>$16.1 \pm 0.4$</td>
</tr>
<tr>
<td>$^{75}$As</td>
<td>$0.27 \pm 0.02$</td>
<td>$0.28 \pm 0.03$</td>
</tr>
</tbody>
</table>
procedures based on an evolutionary algorithm to provide knowledge about intensities, NMR parameters and their distribution, and the associated error margins. The program is based on the work by Meerts [58] and will be described in detail in a forthcoming publication. The algorithm uses a library database of time domain data sets which were generated using SIMPSON.[59, 60] In this way the experimental conditions can be mimicked accurately for each experiment. For each site a group of simulated data sets are added to describe a distribution in interaction parameters. The weight of each set is determined by the selected distribution function, e.g., given by the work of Czjzek [46] and Le Caër and Brand [47] For the Hahn-echo spectra, approximately 1600 datasets were generated based on the experimental rf-field strength and bandwidth. In the simulations, the maximum of the echo was recorded to identify the intensity contribution for each site. For the QCPMG spectra a slightly different approach was followed. Calculating all echoes in a QCPMG experiment for each quadrupolar interaction is too time consuming and therefore only a single echo was calculated assuming ideal pulses. Each subset was Fourier transformed into five absolute simulated spectra with ideal lineshapes but including quadrupolar distributions, which were least square fitted to the absolute, experimental spectrum. To cover all values appearing in the spectra, the quadrupolar interaction parameters of the As[Ga1] and As[Al1] site were varied over a range of $0 \leq \eta \leq 1, 0 \leq C_q \leq 2 \text{ MHz}$ while the As[Al2Ga2] site had a range of $0.9 \leq \eta \leq 1, 31 \leq C_q \leq 35 \text{ MHz}$ and the As[Al1Ga3] and As[Al1Ga4] site $0 \leq \eta \leq 0.1, 31 \leq C_q \leq 35 \text{ MHz}$. In all fits, the cost function was calculated using a normalized, least square summation

$$
\chi^2 = \sum_{i=1}^{n} \left( \frac{f_i}{f_{\text{max}}} - \frac{g_i}{g_{\text{max}}} \right)^2 ,
$$

(2.12)

where $f$ is the experimental spectrum and $g$ the calculated spectrum from the library and $n$ the number of points. The calculations were performed using up to 20 nodes of a high speed cluster based on Sunfire X4100 computers.

### 2.4.4 Density Functional Theory

Electronic structure calculations were carried out to relate quadrupolar interaction parameters to the different cation configurations. The local electric field gradients have been calculated with the first-principles molecular-dynamics programme VASP,[52, 53, 54, 55] using density functional theory and the PAW method[61, 62] following the approach by Petrilli et al.[51] several convergence tests were carried out, in particular to estimate the effect of the semi-core states and compared with state-of-the-art quantum chemical calculations using DALTON[63]. A detailed summary of the convergence test, molecular simulations on small model systems for AlGaAs and the choice of DFT functional, can be found in the supplementary material. Convergence of the results with respect to k-point sampling, kinetic energy cut-off of the plane wave basis set, and lattice relaxation was checked as well. AlAs has an experimental lattice spacing of 0.56695 nm and GaAs of 0.56614 nm, see [42], thus the lattice mismatch for Al0.5Ga0.5As is $\leq 0.1 \%$. Relaxation of the structure resulted in negligible changes ($< 0.002 \text{ nm}$) in the atom positions. All results below were obtained using the PBE functional[64]. The PAW datasets have frozen [Ar], [Ne] and [Ar]3d10 cores for Ga, Al and As respectively. On the basis of these results, we think that the obtained quadrupolar distributions are a good representation for this lattice.
2.5 Results and Discussion

2.5.1 1. $^{75}$As QCPMG analysis

The high quadrupolar moment of $^{75}$As and its strategic anion position in the AlGaAs lattice makes it the most interesting nucleus to probe for information about the symmetry and ordering of the crystal lattice. As detailed in the experimental section, frequency-stepped QCPMG experiments\cite{10, 39, 40, 9} were used to obtain good sensitivity $^{75}$As spectra with signals dispersed over 2 MHz. Figure 2.2 displays the summation of the experimental QCPMG subspectra for each frequency offset for $\text{Al}_{0.297}\text{Ga}_{0.703}\text{As}$ and $\text{Al}_{0.489}\text{Ga}_{0.511}\text{As}$. The spectra show two narrow resonances separated by $\delta = 188 \pm 5$ ppm, in accordance with previous work\cite{65} these lines are assigned to the signals of As[Ga$_4$] and As[Al$_4$] sites having a symmetric first coordination sphere. An arsenic nucleus surrounded by four aluminum or gallium nuclei, has a tetrahedrally symmetric structure and should therefore display no quadrupolar interaction. However, depending on the positions of the cations in the third and higher coordination spheres, there can still exist a (relatively small) EFG. Indeed, in the work by Degen et al.\cite{42} a $C_q = 610$ kHz and $\eta > 0.97$ was determined for As[Ga$_4$] and $C_q = 820$ kHz, $\eta > 0.88$ for As[Al$_4$]. Here we show that these sites can be properly fitted to a Czjzek distribution, with $d = 5$ and average quadrupolar values of $C_q = 610$ and 820 kHz, as were obtained from $^{75}$As nutation NMR experiments\cite{42} The average quadrupolar coupling constants for these two sites were fixed as the fit was not very sensitive to small changes in this parameter.

The wide resonances, not directly observed in the previous study, show distinct quadrupolar features of second-order central-transition powder patterns. A line shape with an asymmetry parameter $\eta$ close to zero is easily identified. The high signal to noise ratio allowed visualization of the small but distinctive features extending from both sides of the spectrum of the spectrum indicating the presence of a species with a high asymmetry parameter. The broad resonances are assigned to $^{75}$As resonances with an asymmetric first coordination shell. Based on a simple point charge model\cite{66} we calculate a quadrupolar coupling constant of approximately 33 MHz for these coordinations. The asymmetry parameter is predicted to be $\eta = 1$ for the As[Al$_2$Ga$_2$] coordination and $\eta = 0$ for the As[Al$_3$Ga$_3$] and As[Al$_3$Ga$_3$] coordinations. The enormous width of the spectrum makes it difficult to determine the chemical shift of these resonances with any accuracy.

The spectra were fitted using an evolutionary algorithm\cite{58} to deconvolute the signals into the contributions from each individual $^{75}$As site as is shown in Figure 2.2. The different quadrupolar subspectra used as library spectra for fitting the QCPMG spectra were calculated assuming ideal non-selective excitation in SIMPSON\cite{59}. The fit with the lowest average cost or $\chi^2$ was found using the model with the least constraints, i.e. using a Gaussian quadrupolar distribution in the $C_q$ and a single $\eta$ value. Although good line shapes are obtained, fitting with a Gaussian distribution in $C_q$ and $\eta$ does not have a physical meaning. Therefore as has been discussed, we used the Czjzek distribution with $d = 5$ to describe the narrow resonances and extended Czjzek distributions for the broad resonances thus taking the effect of the first coordination shell on the EFG tensor into account. Based on some initial simulations and the size of the quadrupolar coupling constant of the As sites with a symmetric first coordination shell, the contribution of the higher coordination spheres was fixed to 715 kHz in the fits of the spectra.
Figure 2.2: (top) $^{75}$As absolute sum of all 24 frequency-stepped QCPMG spectra of Al$_{0.297}$Ga$_{0.703}$As (dotted line) obtained at 18.8T and the simulated spectrum of a GA-based fit using a library of spectra simulated using the SIMPSON package (solid line). The five lower spectra show the contributions from each site. (bottom) The sum of all 22 frequency-stepped QCPMG spectra of Al$_{0.489}$Ga$_{0.511}$As together with the fitted result and the individual contributions of each site. The experimental SNR was $\approx 120$ per frequency step accumulating 5400 scans.

The frequency stepped QCPMG experiment was designed to obtain undistorted lineshapes from very broad quadrupolar resonances at limited rf-field strengths. Here we are faced with the presence of very broad sites with large quadrupolar interactions and narrow lines for the As[Ga$_4$] and As[Al$_4$] resonances experiencing only very small EFGs. Indeed the spectra show some spectral distortions around the center frequency due to truncation of the narrow lines. As the off-resonance behavior of the lines with small ($< 1$ MHz) and large ($> 30$ MHz) quadrupolar interactions differs, adding the off-resonance spectra somewhat affects the shape of the spectrum. The broad resonances of the As[Al$_1$Ga$_3$], As[Al$_1$Ga$_4$] and As[Al$_2$Ga$_2$] coordinations could be fitted very well however, and gave consistent results in fitting the spectra of both the Al$_{0.297}$Ga$_{0.703}$As and Al$_{0.489}$Ga$_{0.511}$As sample. The fit parameters are summarized in table 2.3.

The effective excitation differs significantly for the various sites at different resonance offsets.$^{36, 37}$ Therefore we question the possibility to reliably quantify the relative intensities of the arsenic sites considering spectra obtained at different resonance offsets were added. Moreover, it is too
time consuming to calculate the entire signal response, consisting of the 242 echoes, for each of the
≈ 2000 $C_q$ and $\eta$ values, which are needed for the fitting library, using actual excitation parameters.
To get a reasonable estimate for the molar ratios of the different arsenic coordinations, the on-
resonance QCPMG spectra (i.e. with the excitation frequency in between the narrow lines) were
fitted for each sample. In this case the broadened line shapes were mimicked by using the average
quadrupolar coupling constant and adding a large Gaussian broadening of 50 kHz. The intensities
obtained in this fit were scaled by the relative intensities obtained in a SIMPSON simulation of
a single echo for each site using the actual rf field strengths as used in the experiments. The
results are given in table 2.3. Comparing the intensities from this analysis to the relative intensities
expected for random ordering of the Al and Ga nuclei deviate for both the Al$_{0.489}$Ga$_{0.511}$As and
the Al$_{0.297}$Ga$_{0.703}$As with the discrepancies being largest for the latter sample. In both QCPMG
spectra the intensities of the As[Ga$_4$] and As[Al$_4$] resonances with small quadrupolar interactions
seem to be substantially underestimated.

2.5.2 II. $^{75}\text{As}$ Hahn-echo analysis

Although the QCPMG experiments give good signal to noise ratios for the very wide $^{75}\text{As}$ resonances,
revealing even broad low intensity features at the edge of the lines, the quantification of the relative
intensities in the spectra is considered to be compromised. Therefore we attempted Hahn-echo
experiments at an elevated rf-field strength to get easier processing and calibration of the spectra.
The experimental results, together with unrestrained fits of these spectra are shown in Figures 2.3
and 2.4 for Al$_{0.297}$Ga$_{0.703}$As and Al$_{0.489}$Ga$_{0.511}$As. Indeed the signal to noise of the $x \approx 0.489$
Hahn-echo was a factor 46 lower than a corresponding QCPMG spectrum, but the main spectral
features are similar to those observed in the QCPMG spectra.

The library files used for the GA analysis were obtained from SIMPSON simulations of the Hahn
echo using the parameters as used in the experiments. As before, the As[Ga$_4$] site was fitted with a
Figure 2.4: (top) The experimental $^{75}\text{As}$ Hahn-echo spectrum (18.8 T, 166000 scans, SNR $\sim$ 80) of $\text{Al}_x\text{Ga}_{1-x}\text{As}$, $x=0.489$ (dotted line) together with the fit (solid line). The five lower spectra show the contributions from each site. (bottom) Restrained fit imposing a CuAu order parameter model, where the $S$-parameter was left free to vary and the $x$ could vary within 2%. The relative intensities fitted to $S = 0.01$ and $x = 0.483$. The five lower spectra show the contribution from the individual sites.

fixed Czjzek distribution with $< C_q > = 610$ kHz and $d = 5$, the As[Al$_4$] site with $< C_q > = 820$ kHz and $d = 5$, and as fixed input for the distribution of the extended Czjzek distributions for the As[Al$_n$Ga$_{1-n}$], $n = 1, 2, 3$ sites we used the average quadrupolar coupling constant of the two symmetric sites $< C_q > = 715$ kHz, the EFG principal values $V^{\eta 0}$ and $V^{\eta 1}$ from the first coordination shell of these sites were left free to fit. As is clear from the fits of the $x \approx 0.297$ (Fig. 2.3) and 0.489 samples (Fig. 2.4), the spectral deconvolution using the Czjzek and extended Czjzek distributions works very well for all spectra. The quadrupolar interaction parameters obtained from these Hahn-echo data are in good agreement with those obtained from the QCPMG data. The quadrupolar coupling constant for the As[Al$_2$Ga$_2$] site is slightly lower which is attributed to the less efficient excitation of the broad features at the edges of the Hahn-echo spectra. The relative intensities obtained from the these spectra differ significantly from those estimated from the on-resonance QCPMG spectra. The intensities of the narrow lines seem much more realistic now, but the values obtained from the simulations still differ from those expected for an order parameter model.
2.5. RESULTS AND DISCUSSION

As an alternative we imposed the CuAu order parameter model in the fitting procedure of the $x \approx 0.489$ spectrum, leaving the $S_{\text{CuAu}}$ free to fit and the composition value $x$ free to vary within 2%, which will constrain the five relative intensities. The latter was implemented to allow for experimental errors in the composition $x$, from the growth process. Fig. 2.4 shows the fit of the Al$_{0.489}$Ga$_{0.511}$As spectrum. The best fit was obtained for $S = 0.01$ and $x = 0.483$. Compared to the free fit with $\chi^2 = 0.98$ the $\chi^2$ increased to 2.14, see table 2.3. The restrained fit imposes the relative intensities defined by the long-range order parameter and it was observed that the least square deviation increased. Nevertheless, this restrained fit is considered reasonable, since the spectra show no indication of long range order in the samples in accordance with X-ray data. Using the same the Al$_{0.297}$Ga$_{0.703}$As sample shows a very different picture, however. In this case it proved impossible to fit the relative intensities complying to an order parameter model.

To estimate the reproducibility of the fit procedure, synthetic spectra were generated with random noise of the same order of magnitude and with the same bandwidth as was visible in the experimental spectrum. The standard deviation of the relative intensities due to white noise, did not exceed 2%. The confidence intervals for the relative intensities were determined from the standard deviation of seven different fits, 1% error margin was added to each site to account for systematic errors. The confidence intervals are smaller for the $x \sim 0.489$ sample, caused by the more distinctive shape of the spectrum. $p_1$ and $p_3$ were indistinguishable and considered as one intensity $p_1 + p_3$.

The spectra of both the Al$_{0.489}$Ga$_{0.511}$As and the Al$_{0.297}$Ga$_{0.703}$As sample do not show distinct signs of long-range order. The distributions in quadrupolar interaction parameters clearly indicate positional disorder in the occupancy of the Al and Ga sites in the higher coordination spheres of all the arsenic in the lattice. Remarkably, however, the relative intensities of these sites do not comply with an $S = 0$ situation using the order parameter model as used for the description of XRD data. Although a restrained fit of the $x \approx 0.489$ sample did fit to $S = 0$. For this sample the results show a similar observation as that by Tycko et al.,[43] i.e. that the relative NMR intensities of different C atom coordinations in $A_2B_1 \ldots C$ type materials can be used to set an upper limit to the long range order parameter in such materials. The fitted relative intensities for the $x \approx 0.297$ sample deviate strongly from the order parameter model and could not be fitted to any $S$ (Fig. 2.5). It should be noted that, the order parameter model as used here, only considers the average long range order and does not take any specific short range order into account. Therefore, it is worthwhile to explore further if the NMR spectra contain any information about local order on a nm scale. Short range ordering contains similar surroundings/sites As[Al$_n$Ga$_{4-n}$] $n = 0$-4, but for $n = 1, 2, 3$ each surrounding has a discrete set of tensor orientations (see section DFT).

2.5.3 III. $^{69}$Ga nutation and 3QMAS

To independently verify the random distribution of Al and Ga over the lattice, a series of static nutation experiments were performed for $^{69}$Ga at 14.1 T for the $x \sim 0.297$ sample. In the case of an ordered structure, or domains with high ordering, there should be a Ga resonance without any quadrupolar broadening present in the spectrum. In $^{69}$Ga static spectrum only one (Gaussian) signal is present at $\sim 6$ ppm with respect to GaAs. In a nutation experiment the line shape is dependent on the ratio of the quadrupolar frequency $\nu_Q$ and the rf-field strength $\nu_1$. The nutation
spectra in Figure 2.15 show rather featureless lines, as was also observed earlier for $x \approx 0.489$ by Degen et al.\cite{42} This is attributed to the effect of a distribution in quadrupolar parameters and to some extent the effect of RF inhomogeneity. Degen et al. found a $C_q = 520$ kHz and $\eta > 0.97$ for $x \approx 0.489$. We fitted the data using Czjzek distributions with $d$ ranging from 1 to 5 and for $\sigma = 100$ to 600 kHz. It is verified that the simulated nutation spectra for $\eta \sim 1$ (dashed thin line), or a Czjzek distribution (solid line) do not differ much. Although it was not possible to uniquely fit the nutation data to a specific model, the spectra clearly preclude the existence of a Ga site with a near zero quadrupolar interaction or/and low $\eta$. This rules out the presence of highly ordered domains in this sample.

An additional verification of the absence of well-defined Ga sites in ordered structures comes from $^{69}$Ga static, MAS and 3QMAS spectra. The $^{69}$Ga line width contains different contributions including quadrupolar and dipolar broadening and broadening due to the exchange interaction.\cite{68} At 9.4 T the static Gaussian full width at half maximum (FWHM) is 2.8 kHz, using 15 kHz Magic Angle Spinning (MAS), the shape remains Gaussian with a FWHM of $\sim$1.6 kHz. The second order quadrupolar contribution to the linewidth is of the order of $(3/64) \cdot (C_q^2/\nu_z)$ \cite{69}. With quadrupolar coupling constants up to $\sim$800 kHz this contribution is less than $\sim$300 Hz. Therefore the main contributions to the linewidth originates from a distribution in isotropic chemical shift and/or exchange interaction. This is also clear from the $^{69}$Ga (3Q)MAS spectrum obtained at 14.1T for Al$_{0.297}$Ga$_{0.703}$As shown in Figure 2.7. The broadening of the spectrum mainly extends along the shift axis. From the position of the center of gravity in both directions, $\delta_1 = -5.1$ ppm and $\delta_2 = -7.4$ ppm,
Table 2.3: NMR parameters obtained from fitting the experimental spectra. The reported confidence intervals are standard deviations from 7 fits. The relative intensity of each site is normalized to the echo maximum in the time domain. In the restrained fit, the $S_{CuAu}$ order parameter was left free to fit and converged to $S_{CuAu} = 0.01 \pm 0.01$ and $x = 0.483 \pm 0.004$. The $^{75}$As quadrupolar coupling constant was calculated from the EFG by multiplication with a factor of 0.75925 MHz per $10^{20}$ V m$^{-2}$. An increased $\chi^2$ corresponds to a poorer fit.

an average isotropic chemical shift $\delta_{iso} = -6.0$ ppm and an average quadrupolar induced shift $\delta_{qis} = -1.45$ ppm was determined resulting a quadrupolar product $P_Q = C_Q \cdot \sqrt{1 + \eta^2/3}$ of 730 kHz in accordance with the nutation data. Again there is no indication of a site with a well-defined (small) quadrupolar coupling constant and asymmetry parameter which would be expected for sites in ordered domains in the sample.

2.6 DFT Modeling

To gain more insight in how structural variations translate into NMR parameters, in particular the quadrupolar interaction and its distributions, we need to simulate many different structures and relate these structure to the NMR parameters. It has been shown that a point charge model is not able to properly predict the EFG distributions in these type of systems. A good model should rely on first-principles input data. We address the problem in two ways: first, we make ordered
Figure 2.6: Experimental $^{69}$Ga static nutation spectra obtained at 14.1 T using different rf field strengths for Al$_{0.297}$Ga$_{0.703}$As (dashed thick lines). The solid lines represent SIMPSON simulations of the nutation spectra assuming a Czjzek [46] distribution in the quadrupolar interaction parameters. Shown is the best fit using $d = 5$, $\langle C_q \rangle = 2\sigma = 0.60$ MHz. The dashed thin lines were calculated using $\eta = 1$ and $C_q = 0.80$ MHz.

Figure 2.7: Sheared $^{69}$Ga 3QMAS spectrum obtained at 14.1 T. A $\pi$-filtered 3QMAS spectrum was acquired using rf-field strengths of 120 kHz and 20 kHz for the hard (5.4 respectively 1.8 $\mu$s) and selective (6 $\mu$s) pulses, respectively. The $\nu_1$ dimension was scaled by 9/34 to get an easy interpretable ppm scale. In this convention a hypothetical resonance without quadrupolar interaction has the same shift value in ppm on both axes.

and randomized structural models using supercells, with the compositions $x = 0.5$ and $x = 0.3125$ and calculate their EFGs with DFT. This approach also allows one to access the energetics of these models. Because of the computational cost the number of configurations studied and hence the statistical quality of the EFG distributions is limited. Moreover, only a few values of the order parameter $S$ can be realized. This “supercell model” approach provides a semi-quantitative understanding. In the second approach, called the “multipole model”, we exploit the additivity of EFGs in AlGaAs. This allows for calculating large numbers of structures, high quality statistics and many values of $S$ to be studied. In this part we restrict ourselves to a computation with equal
2.6. DFT MODELING

amounts of Al and Ga present. Finally, we will show that the obtained distributions for \( S = 0 \) concur with the analytical result of the extended GIM, described by Le Caër and Brand.[47]

2.6.1 I. Supercell models

To approximate the distributions observed in the experimental spectra of the \( x \approx 0.489 \) sample by theory, twelve structures with \( x = 0.5 \) were simulated. Cubic-shape supercells were used, containing 16 formula units in a \( 2 \times 2 \times 2 \) arrangement of conventional zinc blende unit cells, \( i.e. \), \( \text{Al}_{16}\text{Ga}_{16}\text{As}_{32} \). Here we discuss the change in orientation of the tensors, as the occupation of the cation lattice goes from full CuAu ordering to a more random arrangement. One structure was created with full CuAu ordering (\( S_{\text{Cu, Al}} = 1 \)) and one with partial high ordering, \( S_{\text{Cu, Al}} = 0.875 \). Ten structural models were created using random positioning of the Al and Ga cations, all with \( S_{\text{Cu, Al}} \leq 0.25 \). The calculated principal \( z \)-axis of the EFG tensor is plotted for each atom in Fig. 2.8. All atoms were kept at their ideal lattice positions.

Full order In a fully ordered CuAu \( \text{Al}_{0.5}\text{Ga}_{0.5}\text{As} \), the only \( ^{75}\text{As} \) site present is \( \text{As}[^{75}\text{Al}_2\text{Ga}_2] \). The principal \( z \)-axis of the EFG tensor of this site always lies in the \( \text{As} \) \( x - y \) plane (under an angle of 45 degrees). The in-plane orientation changes by 180° between adjacent As layers.

Partial order Swapping only two cations in a \( 2 \times 2 \) cell results in a partially disordered but still highly ordered structure, with a small distribution in the principal EFG \( z \)-axis direction for the \( n = 1, 2, 3 \) sites and a spread of \( \Delta \eta = \pm 0.03 \). Of the 32 As atoms are \( n = 1, 3 \) sites. As depicted in the figure, the Principal Axis System (PAS) of the \( \text{As}[^{75}\text{Al}_2\text{Ga}_3] \) \( (n = 1) \) or \( \text{As}[^{75}\text{Al}_3\text{Ga}_1] \) \( (n = 3) \) EFG tensors have their \( z \)-axis oriented along any body diagonal of a cube, \( i.e. \) in one of 4 possible directions. The main difference between \( \text{As}[^{75}\text{Al}_2\text{Ga}_3] \) and \( \text{As}[^{75}\text{Al}_3\text{Ga}_1] \) is the positive/negative sign of the quadrupolar coupling. The principal \( z \)-axis of an \( \text{As}[^{75}\text{Al}_2\text{Ga}_2] \), \( n = 2 \) EFG tensor has 6 possible orientations along all face diagonals of a cube.

Random In a random lattice the three sites with \( n = 1, 2, 3 \) occur with different relative intensities and the EFG distribution within all sites is much stronger. Ten different random models were used to estimate the distributions in the tensor values. In Fig. 2.9 we approximate the distributions for the \( n = 1 \) and \( n = 3 \) sites with a Gaussian-type distribution as used by Jäger and coworkers[44]. Although the simulated EFG data roughly follow that of a Gaussian distribution, the statistics do not allow a definite conclusion on the shape of the distribution, \( i.e. \) we cannot decide whether it is a Gaussian. Indeed, on physical grounds we do not expect a Gaussian distribution. Evidently we need a model that allows for higher quality statistics (see next section). \( \text{As}[^{75}\text{Al}_4] \) and \( \text{As}[^{75}\text{Ga}_4] \) sites are even more rare in the generated structures, so we do not attempt to fit their distributions with any functional form.

The averages and standard deviations of the \( V_{zz} \) and \( \eta \) distributions for \( x = 0.5 \) are listed in table 2.5. Similar calculations were carried out for the composition with \( x = 0.3125 \) as summarized in table 2.6. Inspecting the tables, we see that for both compositions the agreement of the average \( ^{75}\text{As} \) \( V_{zz} \) and \( \eta \) with the experimental results is reasonable for the random models, for all \( n = 0 \ldots 4 \). For
full CuAu order

partial order

random

Figure 2.8: $2 \times 2 \times 2$ (conventional unit) cells of a Al$_{0.5}$Ga$_{0.5}$As lattice containing 64 atoms. The horizontal layers from bottom to top are Al (blue), As (green), Ga (red), As, Al, As, Ga, As. The arrows display the direction of the $V_{zz}$ principal EFG tensor direction for each atom. (top) fully ordered lattice with $S_{\text{CuAu}} = 1$, (middle) partially ordered lattice with $S_{\text{CuAu}} = 0.875$, (bottom) randomly ordered lattice with $S_{\text{CuAu}} \leq 0.25$. 
the $(V_{zz})$ of the $n = 0$ and $n = 4$ sites the relative difference between calculation and experiment is larger, with calculations overestimating the average EFGs. We have to keep in mind that these EFGs are very small, since they are caused by distant coordination shells. The neglect of the contributions of the arsenic core states might explain this discrepancy (see supplementary information). For $^{69}$Ga the agreement for $x = 0.5$ also seems good, at least as far as the average $V_{zz}$ is concerned. The average $^{27}$Al $V_{zz}$ is considerably underestimated in these calculations, however. This is probably also related to the neglect of core contributions (see supplementary information).

Table 2.4 (upper part) summarizes the calculated total energies for the $(x = 0.5)$ structures displayed in Fig. 2.8. The random structures all have lower total energy than the fully and partially ordered structures. The energy differences are small: $\Delta E \approx 0.04$ eV/64 atoms = 0.6 meV/atom. So we do not observe a significant thermodynamic driving force for ordering.

For the $x = 0.3125$ composition perfect CuAu ordering is not possible. Therefore, we compare the random structures with several ordered models with $S \neq 1$. One of the ordered models has the
lowest total energy, but the differences in energy with other structures are very small. Keeping in mind that there is also an entropic contribution favoring disorder, we again cannot conclude that there is a tendency towards ordering.

2.6.2 II. Multipole Model

As good statistics requires a large number of configurations, we need a very fast method to calculate the EFGs for each new configuration. Below we first describe this method, provide a physical justification, give details on generation of the configurations and analyze the results. This model reproduces the absolute EFG tensor values with an accuracy of \( \sim 10\% \), compared to an independent direct DFT calculation.

We start with a single DFT calculation on a large cubic super cell consisting of \( 4 \times 4 \times 4 \) conventional zincblende unit cells. All cations are Ga, except for one, \( \text{i.e.} \), the cell has composition AlGa\(_{255}\)As\(_{256}\). The DFT calculation yields the EFG tensors for all 256 As atoms so that we know the As EFG as a function of \( r_{\text{AsGa}} \), the vector from Ga to As. For any possible cell with composition Al\(_{x}\)Ga\(_{256-x}\)As\(_{256}\) we calculate the EFGs by multiple addition: For each Ga we add its contribution to the As EFGs at displacements \( r_{\text{AsGa}} \) using the result of the single DFT calculation. Once the contributions due to all Ga’s have been added, the As \( V_{zz} \) and \( \eta \) are obtained by diagonalization. This procedure is very fast, as it obviates the need for a separate DFT calculation for each different atomic configuration. It can be somewhat refined at negligible computational cost. The distributions \( P(|V_{zz}|, \eta) \) are modeled as a function of the order parameter \( S_{CuAu} \). On the computer we generate many, \( 3 \times 10^6 \), configurations by randomly placing cations in the \( 4 \times 4 \times 4 \) unit cell. For each configuration we determine the order parameter \( S_{CuAu} \) from the definition in Eq. 2.1 and then \( V_{zz} \) and \( \eta \) for all atoms. Counting the number of occurrences of the \( (V_{zz}, \eta) \) values then yields the quadrupolar distributions as displayed in Fig. 2.11.

Now let us consider the assumptions that go into this procedure. Suppose we interchange one Al for a Ga atom in Al\(_{x}\)Ga\(_{1-x}\)As. In first order only the polar bonds between the Al/Ga and its 4 neighboring As are affected. The charge redistribution preserves the local tetrahedral symmetry, hence the leading order induced charge moment will be that of an octopole. These octopole (and higher) terms will give rise to an electric field at nearby As sites. The field, in turn, will be screened by the other atoms on the Al\(_{x}\)Ga\(_{1-x}\)As lattice. This screening is described by the microscopic dielectric function \( \varepsilon(r, r') \). In our approach, we implicitly assume this function is independent of the local chemical composition (indeed this is our central assumption). This is reasonable as the (macroscopic) dielectric constants of AlAs and GaAs do not differ much \( (\varepsilon_{\infty} = 8.2 \) respectively \( \varepsilon_{\infty} = 10.8 [71])\). We have also checked this assumption by recalculating the EFGs with DFT for a limited number of random configurations (in smaller super cells). Note that we also neglect the effect of local atomic relaxations. This is justified as the lattice match between AlAs and GaAs is nearly perfect and structural relaxations are very small.

In Fig. 2.10 the arsenic \( V_{zz} \) as obtained by DFT in the AlGa\(_{255}\)As\(_{256}\) and Al\(_{255}\)GaAs\(_{256}\) super cells is plotted as a function of the distance to respectively the Al or Ga atom. Note that only beyond the third As shell the contributions to the \( V_{zz} \) become very small. This occurs at a distance
well below half of the size of the super cell (2.25 nm / 2). So our super cell is chosen sufficiently large that spurious contributions from periodic images are avoided.

Remarking that the screening is dominated by the atoms in the first shell, we can improve our modeling of the As[Al] sites. Based on a DFT calculation with a single Ga (Al$_{255}$GaAs$_{256}$, called “Ga in a sea of Al”) we correctly describe the screening by the first shell, whereas with the calculation based on AlGa$_{255}$As$_{256}$ (“Al in a sea of Ga”) all first shell atoms are Ga. The latter would be more appropriate for the As[Ga] sites. More information on the difference between the “Ga in a sea of Al” and “Al in a sea of Ga” results can be found in the supplementary information.

As each configuration of Al$_{128}$Ga$_{128}$As$_{256}$ yields a specific EFG and $\eta$, an EFG distribution can be constructed relatively fast from many occurrences with similar order parameters $S_{CuAu}$. Configurations that do not match the “stoichiometry” constraint Al$_{128}$Ga$_{128}$As$_{256}$ are discarded. The configurations are sorted by $S_{CuAu}$ that is calculated using Eq. 2.1.

Fig. 2.11 shows the variation in the As[Al$_{1}$Ga$_{4-n}$] EFG distributions, as calculated with the “multipole model” for different CuAu order parameters $S_{CuAu}$. As $S$ becomes larger, in general, the average $V_{zz}$ and $\eta$ values increase. In the lower $S$ range, the distributions are rather insensitive to $S$ (compare the $S = 0$ and $S = 0.5$ curves). Increasing $S$ to 0.5, all $V_{zz}$ distributions become more symmetric, except for As[Al$_{2}$Ga$_{2}$] which develops a pronounced asymmetry. For higher $S$, a pattern with shoulders and “spikes” develops. A similar observation was described analytically in the work of Le Caër et al. [47] (their figures 4 and 5). The quadrupolar distributions for the $n = 0, 4$ sites can be described with Czjzek distributions for $d = 5$ and $S = 0$. $V_{zz}$ of the $n = 1 \ldots 3$ sites are dominated by the atoms in the first coordination shell of the arsenic and the average $V_{zz}$ typically changes by $\sim 3\%$ going from $S = 0$ to $S = 1$ and the distribution narrows.

As expected, the $n = 0$ and $n = 4$ As site provide a much more sensitive probe to the degree of disorder, and a concomitantly weaker EFG (Fig. 2.12). The degree of (dis)order has an even more dramatic impact on the Ga distributions: not only does the average $V_{zz}$ increase from $\sim 1.0 \times 10^{20}$ V/m$^2$ for $S = 0$ to $\sim 1.8 \times 10^{20}$ V/m$^2$ for $S_{CuAu} = 1$ (an 80% increase) but also the width of the distribution is reduced by almost an order of magnitude. The wild oscillations in

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**Figure 2.10:** Principal EFG component $V_{zz}$ for $^{75}$As as a function of the distance to a Ga or Al atom in the AlGaAs lattice. The data were calculated using a Al$_{255}$GaAs$_{256}$ super cell, referred to as "Ga in a sea of Al" (dotted line) or a AlGa$_{255}$As$_{256}$ (solid line) super cell, "Al in a sea of Ga". In the first shell $V_{zz}$ (not shown) attains values of $\pm 43.6 \times 10^{20}$ V/m$^2$. The curves are a guide to the eye.
Figure 2.11: $V_{zz}$ (left) and $\eta$ (right) distributions of the different arsenic sites in $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ for different order parameters $S_{Cu, Au} = 0, 0.5, 0.75, 0.94$ as obtained from DFT-based modeling of a $\text{Al}_{128}\text{Ga}_{128}\text{As}_{256}$ super cell. The distribution in the quadrupolar parameters for the $\text{As}[\text{Al}_4]$ site was simulated using the “Ga in a sea of Al” model, all other sites were calculated using the “Al in a sea of Ga” approach.
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![Graphs showing V_{zz} and \eta distributions for different order parameters S_{Cu_Au} in (0, 0.5, 0.75, 0.94, 1).](image)

**Figure 2.12:** $V_{zz}$ (left) and $\eta$ (right) distributions at the Al and Ga sites in Al$_{0.5}$Ga$_{0.5}$As for different order parameters $S_{Cu_Au} = 0, 0.5, 0.75, 0.94$ and 1 as obtained from DFT-based modeling in an Al$_{128}$Ga$_{128}$As$_{256}$ super cell. For $S = 1$ all occurrences have $\eta = 0$. The Ga distribution was simulated using "Al in a sea of Ga". The Al distribution was simulated using the "Ga in a sea of Al" model.

These $\eta$ patterns might be attributed to an insufficient number of configurations, as the number of configurations decreases with increasing $S$.

2.6.3 III. The Extended GIM Model

We will now focus on the simulations for $S = 0$. As shown in the upper figure of Fig. 2.13, for a lattice with random order, the distribution in the quadrupolar parameters of As[Ga$_4$] and As[Al$_4$] derived from the “multipole model” perfectly match a Czjzek distribution with $d = 5$ and an average quadrupolar constant $\sigma$. Such distributions are isotropic and rotation invariant. The quadrupolar distributions obtained for the $n = 1, 2, 3$ sites for the $S = 0$ structures could be matched when a defined first shell tensor was added the distributions in EFG due to the disorder in the higher coordination sphere as described earlier. In fact, these distributions also matched the analytical extended GIM as described by Le Caër and Brand [47]. The $n = 1$ and $n = 3$ distributions have $\eta(0) = 0$ and match with their Eq. 61, see bottom figure of Fig. 2.13. The $n = 2$, i.e., $\eta(0) = 1$ fit in Fig. 2.13 cannot be obtained with a simplified analytical expression, such as Eq. 61 in Le Caër and Brand. This distribution was obtained numerically, by integrating Eq. 2.10 over all three Euler angles ($0 \leq \alpha < 2\pi$, $0 \leq \beta < \pi$, $0 \leq \gamma < 2\pi$).

We also modeled the EFG distributions of the Ga and Al sites for the disordered $S = 0$ situation using the additivity model of the tensor values, applying the “Al in a sea of Ga” or “Ga in a sea of Al” approach. These distributions appeared to be more complex and do not follow the regular or
Figure 2.13: Overlayed contour plots of the probability density function in quadrupolar coupling parameters $P(V_{zz}, \eta)$ generated from DFT calculations and using the analytical expression from Czjzek [46] and Le Caer and Brand [47]. The dotted lines are the DFT-derived data using the multipole model for $S = 0$ of As[Ga4] (more noisy lines, top plot), As[Al2Ga2] (middle) and As[Al1Ga3] / As[Al3Ga1] (bottom). The solid lines show the Czjzek distribution with an average field gradient of $1.19 \times 10^{20}$ V/m$^2$ and $d = 5$ (top), the extended Czjzek distribution and a first shell tensor $V^{01} = 33.1$ MHz, $\eta(0) = 1$ (middle) and $V'^{00} = 33.1$ MHz $\eta(0) = 0$ (bottom). All DFT calculations are based on the “Ga in sea of Al” approach.
extended Czjzek distribution. For Ga the overlap with a Czjzek distribution with $d = 5$ is displayed in Fig. 2.14. Even though the cations are randomly positioned, the calculated distribution is more structured than a Czjzek with $d = 5$. We attribute this to the fact that for gallium the distribution mainly originates from the closer, second shell. This is closer than the case of the arsenic $n = 0$ and $n = 4$ sites, where the first and second shell are isotropic. So we conclude that the effect of the closer second shell cannot be modeled with a fully random model such as the Czjzek distribution with $d = 5$.

2.6.4 IV. Comparing Theory and Experiments

The average EFG values can be predicted well using our DFT approach as implemented in the VASP package. For arsenic, we approach the experimental results quite satisfactory: For As[Al$_3$]$_2$, As[Al$_3$Ga$_1$] and As[Al$_2$Ga$_2$] sites the discrepancies between theory and experiment for e.g., $\langle V_{zz} \rangle$ ($\langle V_{q} \rangle$) are substantially below 10 % for both sample compositions $x = 0.5$ and $x = 0.3125$. For the As[Al$_4$] and As[Ga$_4$] sites, the discrepancies are somewhat larger. It should be noted, however, that these EFGs are two orders of magnitude smaller. The differences could be due to small errors arising from the neglect of the response of (deep) core electrons. The limited number of random supercell models that could be generated do not allow to make predictions about the exact shape of the distributions $P(V_{zz}, \eta)$, however. For $x = 0.5$ we showed that the combined EFG distribution of the As[Al$_3$Ga$_3$] / As[Al$_3$Ga$_1$] sites (Fig. 2.9) still had insufficient statistical quality. This distribution was derived from an average of 176 + 113 = 309 different As sites, see table 2.5. For the As[Ga$_4$] and As[Al$_4$] sites we can only average 17 and 14 configurations respectively, so it is really impossible make any statement on the shape of the distribution function $P(V_{zz}, \eta)$ based on this data.

The multipole model with $x = 0.5$ was based on $3 \times 10^6$ configurations, where each configuration was constructed out of 256 As atoms. This allows for reliable statistics, also for the relatively rare As[Al$_4$] and As[Ga$_4$] sites. The additional approximations result in some errors, but all ($n = 0 \ldots 4$) $V_{zz}$ averages are well within the expected $\sim 10 \%$ of the supercell models. The data obtained from the As[Al$_4$] site seems to deviate more, but note that the estimated RMS error in the average, obtained with the supercell models, is $0.33 \text{ MHz}/\sqrt{14} = 0.09 \text{ MHz} \sim 8\%$. With the multipole model, the
Table 2.5: EFG simulations of Al$_{0.5}$Ga$_{0.5}$As compared to experimental results from Degen et al.\cite{42} and to the results of this study. The numbers $A(C)\mu$ represent $A$ = average $C_q$ value in MHz, $C$ = standard deviation of the distribution in MHz, $n$ = number of occurrences in the model. $(C/\sqrt{n}$ represents the accuracy of the mean value in MHz), “-” non-existing entries. The DFT calculations for the super cell models were carried out in a 2 x 2 x 2 unit cell, with 32 arsenic, and a total of 32 (aluminum and gallium) atoms. 10 super cells were used for $x = 0.5$.

<table>
<thead>
<tr>
<th></th>
<th>Theory ($x = 0.5$)</th>
<th>Experiment ($x \approx 0.489$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ordered CuAu supercell model</td>
<td>multipole model</td>
</tr>
<tr>
<td>$C_q$ (MHz)</td>
<td>$S = 1$</td>
<td>$S \sim 0$</td>
</tr>
<tr>
<td>69$^{\text{Ga}}$</td>
<td>0.20 (0) 16</td>
<td>0.54 (0.20) 160</td>
</tr>
<tr>
<td>Al</td>
<td>0.046 (0) 16</td>
<td>0.16 (0.06) 160</td>
</tr>
<tr>
<td>As[Ga$_4$]</td>
<td>-</td>
<td>0.71 (0.23) 17</td>
</tr>
<tr>
<td>As[Al$_4$]</td>
<td>-</td>
<td>1.07 (0.33) 14</td>
</tr>
<tr>
<td>As[Al$<em>{1/3}$Ga$</em>{3/1}$]</td>
<td>-</td>
<td>32.90 (0.59) 176</td>
</tr>
<tr>
<td>As[Al$_2$Ga$_2$]</td>
<td>34.7 (0) 32</td>
<td>33.20 (3.07) 113</td>
</tr>
</tbody>
</table>

$^a$Czjzek distribution with $< C_q > = 2.0 \cdot \sigma$ for $d = 5$; $^b$Assumed Czjzek distribution with $d = 5$ and $C_q$ from the rotation data from Ref. \cite{42}; $^c$Extended Czjzek distribution. Note that the compared values are average EFGs and not first shell EFGs, although they do not differ much.

Table 2.6: EFG simulations of Al$_{0.3}$Ga$_{0.7}$As compared to the experimental results. The left column displays the results from a single simulation with the highest ordering, the second column displays the result from 3 partially ordered simulations, the third column from 11 random simulations.

<table>
<thead>
<tr>
<th></th>
<th>Theory ($x = 0.3125$)</th>
<th>Experiment ($x \approx 0.297$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ordered CuAu Part. ord. supercell models</td>
<td></td>
</tr>
<tr>
<td>$C_q$ (MHz)</td>
<td>$S_{\text{CuAu}} = 0.375$</td>
<td>$S_{\text{CuAu}} = 0.125$</td>
</tr>
<tr>
<td>69$^{\text{Ga}}$</td>
<td>0.54 (0.14) 22</td>
<td>0.47 (0.19) 66</td>
</tr>
<tr>
<td>$^{27}$Al</td>
<td>0.14 (0.06) 10</td>
<td>0.09 (0.03) 30</td>
</tr>
<tr>
<td>As[Ga$_4$]</td>
<td>0.81 (0.35) 12</td>
<td>0.75 (0.25) 28</td>
</tr>
<tr>
<td>As[Al$<em>{1/3}$Ga$</em>{3/1}$]</td>
<td>33.1 (0.27) 8</td>
<td>33.1 (0.37) 24</td>
</tr>
<tr>
<td>As[Al$_2$Ga$_2$]</td>
<td>34.5 (0.71) 12</td>
<td>34.6 (0.74) 44</td>
</tr>
</tbody>
</table>

$^a$m MQMAS and rotation. $^c$Extended Czjzek distribution.

discrepancy between theory and experiment for As[Al$_4$] is reduced to $\sim 15\%$. The As[Ga$_4$] has, unfortunately, increased a bit to $\sim 25\%$. As these EFGs are very weak, we think these results are very reasonable.
2.7 CONCLUSIONS

The main advantage of the multipole model is that we can now study the distribution functions themselves, even for the difficult sites As[Al\textsubscript{4}] and As[Ga\textsubscript{4}]. We found (Fig. 2.13) that the latter are accurately described by Czjzek distributions with $d = 5$. Thus we provide a first-principles basis to support this model. Using these results to describe the “amorphous” background, we then find that the EFG distributions of the As[Al\textsubscript{2}Ga\textsubscript{3}], As[Al\textsubscript{3}Ga\textsubscript{1}] and As[Al\textsubscript{1}Ga\textsubscript{2}] sites are all accurately described by the extended Czjzek distribution.

2.7 Conclusions

A judicious choice of rf-coil diameter makes it possible to observe $^{75}$As spectra from thin film material of AlGaAs grown by MOCVD. Reducing the coil diameter provides the sensitivity to study the limited amount of material available from a single film. Additionally the small diameter of the coil enables the generation of rf-fields large enough to efficiently excite the entire bandwidth of the arsenic spectrum. Frequency-stepped QCPMG spectra and single Hahn-echo experiments both reveal the presence of five resonances assigned to As[Al\textsubscript{n}Ga\textsubscript{1−n}], $n = 0$-4 with NMR parameters mostly depending on the symmetry of the first coordination shell. The quadrupolar coupling constant varies from less than 1 MHz for the symmetric $n = 0$ and $n = 4$ coordinations, to over 30 MHz for the asymmetric $n = 1, 2, 3$ coordinations. Using an evolutionary algorithm, the spectra can be decomposed into the individual contributions from the different As resonances. The frequency-stepped QCPMG data allow the most accurate determination of the quadrupolar interaction parameters; this is of particular importance for the As[Al\textsubscript{2}Ga\textsubscript{2}] site whose low intensity discontinuities from the $\eta = 0$ second-order quadrupolar powder pattern at the edge of the spectra are most pronounced in the QCPMG spectra. These spectra, containing resonances from sites with small and large quadrupolar interactions can not produce reliable relative intensities for the different sites, however, due to the varying excitation efficiencies for the different sites at varying resonance offsets. The quadrupolar interaction parameters extracted from the Hahn-echo experiments are in accordance with those obtained from the QCPMG data, except for the As[Al\textsubscript{2}Ga\textsubscript{2}] site that comes out slightly smaller. As expected the Hahn-echo experiments are less sensitive compared to the QCPMG data. The advantage of the Hahn-echo data is that it is possible to determine the relative intensities of the As sites.

Imposing an order parameter model on the fits gives a satisfactory solution of $S = 0$ for the Al\textsubscript{0.489}Ga\textsubscript{0.511}As sample, meaning the Al and Ga nuclei are randomly distributed over their lattice sites. For the Al\textsubscript{0.297}Ga\textsubscript{0.703}As material no satisfactory fit using the order parameter model could be obtained. These results indicate that there is no long-range order present in both samples. The structural disorder in the occupancy of the Al/Ga sites is also reflected in the distributions of the quadrupolar interaction parameters of the As sites. The symmetric As[Al\textsubscript{4}] and As[Ga\textsubscript{4}] sites have finite quadrupolar interactions with a distribution which can be described by a Czjzek distribution with uncorrelated Gaussian distributions in the five independent electric field gradient tensor values. This reflects the random disorder in the higher coordination spheres of these Arsenic sites which is isotropic and rotation invariant. For the As sites As[Al\textsubscript{n}Ga\textsubscript{1−n}], $n = 1, 2, 3$ with a mixed first coordination shell, the electric field gradients can be described by a summation of the EFG of the first...
CHAPTER 2. THE ATOMIC ORDERING OF $\text{Al}_x\text{Ga}_{1-x}\text{As}$

coordination sphere to a Czjzek distribution resulting from the disorder in the higher coordination spheres. This "background" Czjzek distribution is identical to the one obtained for the symmetric $\text{As}[\text{Al}_n\text{Ga}_{1-n}]$, $n = 0, 4$ sites.

Field dependent $^{69}\text{Ga}$ MAS NMR data, nutation and 3QMAS spectra of both $\text{Al}_x\text{Ga}_{1-x}\text{As}$ ($x = 0.489$ or $x = 0.297$) samples did not show the presence of Ga species with a zero or very small quadrupolar interaction as would be expected in the case of formation of ordered structures supporting the conclusion of random ordering.

DFT calculations of the electric field gradient tensors based on the PAW method implemented in VASP are in good agreement with the experimental data. As the lattice constants of AlAs and GaAs are nearly equal and their dielectric constants are very similar it is possible to calculate the effects of structural disorder in AlGaAs lattices based on calculations of a single $\text{Al}_{255}\text{Ga}_{8256}$ and $\text{AlGa}_{255}\text{As}_{8256}$ supercell. From these calculations the effect of a Ga or Al on a specific As can be calculated and these contributions can be used in an additive manner when generating large numbers of random or partly ordered structures. The distribution in quadrupolar parameters of the As sites derived from these analyses for randomly ordered materials perfectly match those from the Czjzek (Gaussian isotropic) models used to describe the experimental data. The Ga DFT simulations for $S = 0$ nearly match a Czjzek type distribution with $d = 5$, but the distribution is more complex. In general the calculations predict a shift and narrowing of the distribution in quadrupolar coupling constant with increasing order parameter. Furthermore the calculations show that there is an influence on the local EFG up to the 7th coordination shell, with the first three shells being most dominant.

Our findings of random cation arrangement for $x \approx 0.297$ and $x \approx 0.489$ agrees with earlier studies. Degen et al. found a short-range parameter $S \sim 0.2$ for similar samples on the bases of the intensities of the two symmetric As sites, with $n = 0, 4$. Most studies of long-range order in these semiconductors claim that the order parameter is quite small $S < 0.05$, indicating that clusters of similar ordering are not linked throughout the entire sample. Our data do not fit very well using a long-range order parameter model even for $S = 0$. This might indicate that some short range order exists. Indeed, long and short-range order parameters do not have to be in the same range. Interrupted Al / Ga strings are observed in AlGaAs in an XSTM study.[34] They find a volume fraction of Al strings of only $\sim 0.3\%$ for $x = 0.15$. The presence of Al strings would be observed in our resolved $^{75}\text{As}$ spectra, if the volume fraction of strings is sufficient, roughly $\geq 1\%$. Besides sensitivity, an additional problem for analyzing powdered NMR data is that the distribution in EFG is convoluted with the powder distribution. The EFG tensors of the $\text{As}[\text{Al}_n\text{Ga}_{1-n}]$, $n = 1, 2, 3$ sites have distinct orientations which are modulated by specific order or disorder in the higher coordination shell. Therefore more subtle studies of potential local order in these materials would require the possibility to study a single oriented film, which demands a further increase in volume sensitivity. Miniaturization is a key concept here. We have recently shown advances in this area, using stripline based micro-coil detectors [38].
2.7.1 Acknowledgements

The authors like to thank J. van Os and G. Janssen for technical support; M. Voncken for providing the AlGaAs samples. A. Lipton for his assistance on the Simpson discussion forum, A. Brinkmann and R. Siegel for experimental help and for the assistance with SIMPSON. C. Degen for aiding with the formulas to determine the intensities of the sites and S. Vasa for stimulating discussions. The DFT study is part of the research program of the “Stichting voor Fundamenteel Onderzoek der Materie (FOM)”. Financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (Netherlands Organization for Scientific Research, NWO) is acknowledged for sponsoring the solid-state NMR facility for advanced materials science where the NMR experiments were performed and the Stichting Nationale Computerfaciliteiten (National Computing Facilities Foundation, NCF) for the use of supercomputer facilities.

2.8 Supplementary - The Atomic Ordering of Al$_x$Ga$_{1-x}$As

This supplementary is divided into an experimental NMR section, concerning the QCPMG data and a theoretical DFT part.

2.9 Experimental

Due to the huge breadth of the arsenic spectrum, even at 18.8 $T$, high rf fields are advantageous since they can excite the entire spectrum. Besides the strength of the rf field, special attention is given to the homogeneity over a wide frequency range. To this end a series of reference experiments were performed by measuring the $^{75}$As nutation of a reference GaAs sample. Note that the effective rf field used in this supplementary was 455 kHz, in the manuscript 390 and 625 kHz were used for the QCPMG respectively Hahn-echo.

2.9.1 Effective rf field strength

Fig. 2.15 displays the result from the nutation experiments. The rf field strength was 520 kHz at 820 Watt and reduced only 7.5% -1.5 MHz away from its tuned resonance frequency. To obtain strong rf fields, we need high power levels. At these powers, the build-up and decay time of the pulse are relevant, since the pulses become relatively short. The nutation frequency was determined from the Fourier transformation of the nutation data. The experimental date included pulses with a length up to 20 $\mu$s. At short times, the energy applied to the probe will take some time to build-up (and decay). In effect this reduces the effective rf field determined from the nutation spectrum. For a resonant circuit with $Q \sim 20$, the build-up/decay time is $\tau_b \approx 0.15 \mu$s. The energy build-up in the circuit as a function of time can be described with $P(t) = P_{max} \cdot (1 - e^{-t/\tau_b})$. The rf field scales with the square root of the applied power $\nu_{rf} \propto \sqrt{P}$. We derive $\nu_{rf}(t) = \nu_{rf}^{max} \cdot \sqrt{1 - e^{-t/\tau_b}}$. Substituting $\nu_{rf}^{max} = 520$ kHz from the nutation, the RF field at $t = 0.32 \mu$s reduces to $\approx 488$ kHz, see left figure of Fig. 2.16.
Figure 2.15: A series of reference experiments were performed by measuring the arsenic mutation of GaAs with 820 Watt power at different frequency offsets. The profile confirms the Q factor of the probe of ~20. The maximum rf field strength was 520 kHz.

Figure 2.16: (left) Experimental pulse time build-up and decay. (right) Frequency-stepped-whole-echo QCPMG on $^{75}$As, echo time $\tau = 140$ $\mu$s, $\tau_{acq} = 125$ $\mu$s, 500 points per echo and 242 echoes, $\pi/2 = 0.32$ $\mu$s, $\pi = 0.62$ $\mu$s, $\nu_{rf} = 520$ kHz, power = 820 Watt, spectral width = 4 MHz, frequency step size was 125 kHz. The pulse delay was 1 second. More experimental settings are tabulated in table 2.7.

Table 2.7: Settings of the frequency-stepped QCPMG. In both cases the center frequency was 136.935 MHz.

<table>
<thead>
<tr>
<th></th>
<th>Al$<em>{0.297}$Ga$</em>{0.703}$As</th>
<th>Al$<em>{0.489}$Ga$</em>{0.511}$As</th>
</tr>
</thead>
<tbody>
<tr>
<td>acquisitions</td>
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<td>5.400</td>
</tr>
<tr>
<td>number of frequencies</td>
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<td>22</td>
</tr>
<tr>
<td>freq. range (MHz)</td>
<td>135.310 ... 138.185</td>
<td>135.435 ... 138.060</td>
</tr>
<tr>
<td></td>
<td>-1.625 ... 1.250</td>
<td>-1.500 ... 1.125</td>
</tr>
</tbody>
</table>

2.9.2 QCPMG Analysis

We applied a frequency-stepped QCPMG to the two Al$_x$Ga$_{1-x}$As samples. The QCPMG pulse sequence is displayed on the right side of Fig. 2.16. The center frequency $^{75}$As QCPMG signal of $x \sim 0.489$ was first simulated. The simulated signals from the echo train were added and it was verified that the relative echo intensity from the two central sites, $n = 0, 4$ dropped to $\approx 60\%$ at the 242$^{th}$ echo, while the $n = 1, 2, 3$ sites refocused almost for 100% . The quadrupolar coupling from both sites is very different, thus it is not possible to refocus all sites and the 180 degree echo mostly
selectively focuses the intensity from the $n = 1, 2, 3$ sites.

In five simulations we determined the theoretical $T_2$ projection decays solely due to quadrupolar evolution. This decay fitted reasonably to a single exponent, for $n = 0, 1, 2, 3, 4$ we derived 16.4, 20.8, 12.9, 20.8, 25.0 ms. Experimentally the decay was stronger $\sim 8$ ms, see Fig. 2.17.

Now we consider the off-resonance behavior. In the SIMPSON simulations, we simulated one single whole-echo for all the sites and all the off-resonance frequencies $(\frac{n}{2^y}\tau_s-\tau_{acq}/2-\pi^x-\tau_{ACQ}^x)$, with selective pulse times and the delay time $\tau_s = \tau - \tau_{acq}/2 - t_{90}$. $I_{1m}$ was used as detection operator and the -1 coherence was filtered out after the 90 and 180 degree pulse. The off-resonance, single echo spectra were simulated using $\eta = 1$, $C_q = 610/820$ kHz for $n = 0, 4$ and $\eta = 0.06/0.94$, $C_q = 33.4$ MHz for $n = 1, 2, 3$. To account for broadened quadrupolar interactions, these spectra were broadened by convolution with a Gaussian function. In agreement with our expectations considering the reduced rf field due to the short pulse times, the fits of each frequency significantly improved when the simulated RF field was reduced from 520 kHz (determined from nutation) to 455 kHz (the effective rf field from reduced pulse time). The corresponding simulated, effective pulse times were 0.27 and 0.54 $\mu$s. The effective rf field of 455 kHz is close to the predicted 488 kHz, on the basis of the pulse build-up time.

The fits of the $x \approx 0.489$ spectra are displayed in Figure 2.19. Clearly, the shape and relative intensities of the spectra are affected by the quadrupolar distribution, the off-resonance frequency, the $T_2$’s and the echo train. The central and satellite intensities have to be considered to calculate the relative intensities. Here, they are incorporated in the SIMPSON output.

In Fig. 2.18 the fitted relative intensities are plotted at different frequency offsets. The Figure shows that the five relative intensities were not constant but dependent on the off-resonance frequency. Since only one echo is simulated, it is likely that the off-resonance evolution of the 180
Figure 2.18: The data points are the relative intensities as a function of the off-resonance frequency, fitted to a second order polynomial \( \exp_i \) (dotted line). The solid lines \( p_i \) are the theoretical relative intensities for \( S = 0 \) and \( x = 0.298 \) (left), \( x = 0.487 \) (right).

degree echo-train could be responsible different relative intensities per frequency. The \( n = 0.4 \) sites had near zero relative intensity around \( \pm 1.0 \) MHz. Although, the single echo simulation was able to predict the shape and the relative intensities around the center frequency, the relative intensities far off-resonance were in disagreement with the experiment. Because the off-resonance relative intensities were not correct, we use the (close to) on-resonance data and relate the relative intensities to the order parameter \( S \). In the figure, the solid, horizontal lines show the relative intensities for the best \( S_{CuAu} \) / \( S_{CuPt} \) and \( x \). The best fit to the \( x \approx 0.489 \) data was with \( S = 0 \) and \( x = 0.487 \). This \( x \) is within the allowed 0.5% tolerance. Even if the relative intensities from five fits around the center frequency are averaged, the result is similar. For \( x \approx 0.489 \) we obtain a low order parameter \( S \), in other words random arrangement of the cations.
Figure 2.19: Off-resonance behavior of the absolute QCPMG spectra. The plotted, absolute simulated spectra were acquired using a single echo and a single quadrupolar interaction. The simulated sites with $C_q = 33.5$ MHz were broadened using a Gaussian convolution of 50 kHz for $n = 1, 3$ and 80 kHz for $n = 2$. 
2.10 Density Functional Calculations

This section gives (a) a brief description of the implementation of the EFG calculation in VASP [52, 53, 54, 55], (b) provides test calculations on solid state models of Al$_x$Ga$_{1-x}$As using VASP with various PAW projector sets, (c) provides test calculations on molecular models for Al$_x$Ga$_{1-x}$As using both VASP and the quantum chemical package DALTON [63], and (d) provides additional data on the “multipole model”. The main objective of (b) and (c) is to estimate the influence of core states.

Similarly to pseudopotential methods, in the projector-augmented-wave PAW method [61, 62] the core electrons are frozen and removed from the electronic structure calculation. The Kohn-Sham states and the charge density are represented on a rather coarse-grained grid. Contrary to a pseudopotential method, wherein the orthogonalisation to the core states is removed, the PAW method uses an augmentation procedure to fully describe the nodal structure of Kohn-Sham states, charge density and potential. Moreover, it is possible to “unfreeze” shallow core states so that also their contribution to the EFGs can be calculated.

2.10.1 EFG theory & implementation

The EFG calculation was implemented following Petrilli et al.[51] The central quantity to be calculated is the traceless EFG tensor

\[ V_{ij} = \left( \frac{1}{3} \delta_{ij} \nabla^2 - \partial_i \partial_j \right) v \]

that is to be evaluated at each nucleus. Here \(i\) and \(j\) denote the Cartesian coordinates. In the PAW method the electrostatic potential \(v\) is a sum of three contributions:

\[ v(r) = \tilde{v}(r) - \sum_R \tilde{v}_R^\dagger(r) + \sum_R v_R^\dagger(r) \]

(2.14)

The soft potential \(\tilde{v}\) is augmented within the PAW spheres centered at the nuclear sites \(\langle R\rangle\), where the soft on-site (one-center) potentials \(\tilde{v}_R^\dagger(r)\) are replaced by their all-electron counterparts \(v_R^\dagger(r)\).

The soft potential \(\tilde{v}\) is obtained via the Poisson equation from the soft charge density on the FFT grid. Its gradients are evaluated as a summation in reciprocal space at exactly the nuclear positions \(r \rightarrow R\). The contribution from the ionic nuclei is absorbed into the soft charge density as Gaussians centered at the atomic positions.

Both on-site terms \(\tilde{v}_R^\dagger\) and \(v_R^\dagger\) consist of radial functions represented on a logarithmic grid multiplied by real spherical harmonics \(Y_L\):

\[ v_R^\dagger(r) = \sum_L v_{R,L}^\dagger(|r - R|)Y_L(r - \mathbf{R}) \]

(2.15)

Only the terms with angular momentum \(l = 2\) contribute to the EFG and require evaluation of quantities \(v_{R,L}^\dagger(|r - R|)|r - R|^2\) in the limit \(|r - R| \rightarrow 0\). These are obtained by extrapolation from the first grid points of the logarithmic mesh. More detail on the method can be found in the paper by Petrilli et al.[51] that we closely follow.

Several test calculations were carried on various molecular and solid state systems. Here we just report some of the calculations on TiO$_2$ in table 2.8. We use the same geometry as Petrilli et al. Ti
2.10. DENSITY FUNCTIONAL CALCULATIONS

<table>
<thead>
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<th>$V_{xx}$</th>
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<td>PAW$^c$</td>
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</table>

Table 2.8: Rutile TiO$_2$ EFG components (V/Å$^2$). Cell and positional parameters are from Ref. [51], table III. All PAW calculations: Ti 3s and 3p treated as valence electrons. LAPW$^a$ & PAW$^a$, Petrilli et al. [51]; PAW$^b$, VASP standard potentials; PAW$^c$, VASP optimized potentials.

3s and 3p states were treated as semi-core states. Standard PAW Potentials as supplied with the VASP package were used, as well as highly optimized very accurate projector sets. The calculations were carried out in the LDA.

2.10.2 Convergence tests on ordered Al$_x$Ga$_y$As crystals

Several convergence tests were carried out, most of them using the LDA, in particular to estimate the effect of the semi-core states. We used a tetragonal and cubic cells with compositions AlGaAs$_2$, AlGa$_3$As$_4$ and Al$_3$GaAs$_4$. This allows to test with various As first coordination shells: 2 Al and 2 Ga in case of AlGaAs$_2$, 1 Al and 3 Ga in case of AlGa$_3$As$_4$ and 3 Al and 1 Ga in case of Al$_3$GaAs$_4$. The lattice constant was $a = 5.6394$ Å and atoms were kept fixed at their positions on an idealized zincblende lattice. Results are summarized in tables 2.9, 2.10 and 2.11.

The test results show that the Ga 3d states cannot be kept in the frozen core, but need to be treated as valence. They do not only affect the Ga EFG but also the As EFG. The Ga 3p states also have a substantial effect on the small Ga EFG. The effect of the 3p states, that are 90 eV below the valence band edge, on the Ga EFG is considerably larger (~30 %) than the effect of the shallow Ga 3d core states (~6 %). For Al the 2p core states also give rise to a large relative effect: unfreezing the 2p states (about 60 eV below the valence band edge) reduces the small Al EFG by roughly a factor 2 in AlGaAs$_2$ and 4 in Al$_3$GaAs$_4$. For AlGa$_3$As$_4$ their relaxation even has a small effect on the Ga EFG. The effect of the arsenic 3d states is rather small: although in an absolute sense it is comparable to the core effects of Al and Ga, it only changes the arsenic EFG by one percent.

In the PAW method it is difficult to include core states deeper than those considered above. It requires good scattering over such a wide energy range, hence inclusion of many projector functions, that ghost states start to occur. In order to assess the effect of the frozen core approximation, molecular calculations were performed of small model systems, comparing the PAW method and all-electron results obtained with a quantum chemical package.
Table 2.9: Electric field gradients $V_{zz}$ and asymmetry parameters $\eta$ calculated with various projector sets for AlGaAs$_2$. The frozen core states are listed. *As_d_GW. †Al_h (used for the calculations).

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Ga</th>
<th>As</th>
<th>$V_{zz}$ (V/Å$^2$)</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LDA</td>
<td>[Ne]</td>
<td>[Ar]</td>
<td>3d$^{10}$</td>
<td>[Ar]</td>
<td>3d$^{10}$</td>
</tr>
<tr>
<td></td>
<td>[Ne]</td>
<td>[Ar]</td>
<td></td>
<td></td>
<td>[Ar]</td>
</tr>
<tr>
<td></td>
<td>1s$^2$2s$^2$</td>
<td>[Ar]</td>
<td></td>
<td></td>
<td>[Ar]</td>
</tr>
<tr>
<td></td>
<td>[Ne]</td>
<td>[Ar]</td>
<td></td>
<td></td>
<td>[Ar]</td>
</tr>
<tr>
<td></td>
<td>[Ne]</td>
<td>[Ne]$^3s^2$</td>
<td>[Ar]</td>
<td>3d$^{10}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1s$^2$2s$^2$</td>
<td>[Ne]$^3s^2$</td>
<td>[Ar]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

|       | [Ne]| [Ar] | [Ar]|3d$^{10}$ |       | 0.031  | -0.44   | -50.0 | 0.92 |

|       |       | [Ar]| [Ar]|3d$^{10}$ |       | 0.11   | -0.50   | -45.4 | 0.93 |
|       |       | [Ar]|      |          | [Ar]|3d$^{10}$ | 0.13   | -0.46   | -45.3 | 0.93 |

Table 2.10: Electric field gradients $V_{zz}$ calculated with various projector sets for AlGa$_3$As$_4$. The frozen core states are listed. $V_{zz,Al} = 0$, $\eta_{Ga} = \eta_{As} = 0$.

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Ga</th>
<th>As</th>
<th>$V_{zz}$ (V/Å$^2$)</th>
<th>Ga</th>
<th>As</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LDA</td>
<td>[Ne]</td>
<td>[Ar]</td>
<td>3d$^{10}$</td>
<td>[Ar]</td>
<td>3d$^{10}$</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td>[Ne]</td>
<td>[Ar]</td>
<td></td>
<td></td>
<td>[Ar]</td>
<td>3d$^{10}$</td>
</tr>
<tr>
<td></td>
<td>1s$^2$2s$^2$</td>
<td>[Ar]</td>
<td></td>
<td></td>
<td>[Ar]</td>
<td>3d$^{10}$</td>
</tr>
<tr>
<td></td>
<td>[Ne]</td>
<td>[Ar]</td>
<td></td>
<td></td>
<td>[Ar]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[Ne]</td>
<td>[Ne]$^3s^2$</td>
<td>[Ar]</td>
<td>3d$^{10}$</td>
<td></td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>1s$^2$2s$^2$</td>
<td>[Ne]$^3s^2$</td>
<td>[Ar]</td>
<td></td>
<td></td>
<td>0.33</td>
</tr>
</tbody>
</table>

|       | [Ne]| [Ar] | [Ar]|3d$^{10}$ |       | 0.43   | -44.2 |

|       |       | [Ar]| [Ar]|3d$^{10}$ |       |        |

Table 2.10: Electric field gradients $V_{zz}$ calculated with various projector sets for AlGa$_3$As$_4$. The frozen core states are listed. $V_{zz,Al} = 0$, $\eta_{Ga} = \eta_{As} = 0$.

2.10.3 Molecular calculations on small model systems for Al$_x$Ga$_{(1-x)}$As

To assess the effect of the frozen core approximation in the solid state calculations described earlier, molecular calculations were performed on small model systems for Al$_x$Ga$_{(1-x)}$As (Figure 2.20). Model system m1 mimics the environment of the As atom in the solid state, m2 that of Al, and m3 that of the Ga atom. The Al, Ga, and As positions in these model systems occupy the positions these atoms have in the crystal structure, and only the positions of the pseudo-hydrogen atoms (see Fig. 2.20) have been optimized. The basis set used in the calculations of the electric field gradient was the cc-pVTZ basis set, but all functions were un-contracted. The calculations were performed using the LDA functional with DALTON [63]. Scalar relativistic effects were treated using the Douglas-Kroll formalism. * The calculations were also performed with VASP at the LDA level, using

*The effect of the so-called picture change [72] was neglected. For our nuclei this is still a good approximation.
\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
  & Al & Ga & As \ $V_{zz}$ (V/Å²) \\
\hline
  & Al & As \\
LDA & & & \\
\hline
[Ne] & [Ar] & [Ar]3d\textsuperscript{10} & -0.17 & 49.5 \\
1s\textsuperscript{2}2s\textsuperscript{2} & [Ar] & [Ar]3d\textsuperscript{10} & -0.085 & 49.4 \\
\hline
\end{tabular}
\caption{Electric field gradients $V_{zz}$ calculated with various projector sets for Al$_3$GaAs$_4$. The frozen core states are listed. $V_{zz, Ga} = 0$, $\eta_{Al} = \eta_{As} = 0$.}
\end{table}

\textbf{Table 2.11: } The $V_{zz}$ components and core/valence contributions (in V/Å²) to $V_{zz}$ for the As atom of m1, the Al atom of m2, and the Ga atom of m3. \textsuperscript{a}The core orbitals are 1s, 2s, 2p, 3s, and 3p for As and Ga, and 1s and 2s for Al.

potentials where the 3d electrons for As and Ga and the 2p electrons for Al were taken into account, while the other lower-lying orbitals were treated as frozen core ([Ar] core for Ga and As and a 1s\textsuperscript{2}2s\textsuperscript{2} core for Al).

In DALTON, the EFG tensor is calculated as an expectation value $V_{\alpha\beta} = \langle \psi|\hat{V}_{\alpha\beta}|\psi \rangle$, with $\alpha, \beta$ the cartesian components of interest. Thus, the EFG tensor is a sum of (occupied) orbital ($\phi$) contributions: $V_{\alpha\beta} = \sum_{i} N/2 \langle \phi_{i}|\hat{V}_{\alpha\beta}|\phi_{i} \rangle$ ($N$ is the number of electrons). Note that these orbital contributions do not have any direct physical meaning, but that the contribution of the core orbitals to this expectation value of $V$ is an indication of the error introduced by the frozen core approximation. In table 2.12 the calculated $V_{zz}$ component for the nucleus of interest for the three model compounds is shown, together with its core contribution. The non-diagonal form of the EFG tensor for Al and Ga in m2 and m3, respectively, thwarts the simple decomposition in orbital contributions to $V_{zz}$. Therefore, the core contribution to the EFG tensor for these compounds is obtained by subtracting the core contributions to all tensor components before diagonalisation. The difference between the largest eigenvalues of the total EFG tensor and this non-core EFG tensor is taken as the core contribution to $V_{zz}$.

The relative deviations between the VASP and full-molecular results are 3.2% (As), 3.8% (Al) and 2.5% (Ga). Upon application of this ad-hoc core-correction, the relative deviations in $V_{zz}$ values reduce to 0.03% for As, and to 0.3% for Ga. The 1s and 2s Al-core orbitals do not significantly contribute to the $V_{zz}$ value, and the core-correction even deteriorates the agreement between VASP and the full-molecular results. Differences between VASP and DALTON are not only due to the neglect of core relaxation in the former type of calculations; small differences are also expected because of differences in basis set (plane waves vs. atomic centered Gaussians) and a different treatment of relativistic effects. Still, these calculations provide evidence that core contributions can be significant for As (3.7%) and Ga (2.1%). Hence, EFG calculations using the frozen core approximation are not expected to be more accurate than ca. 5%.
\[ Z_H = 1.25 \]
\[ Z_H = 1.25 \]
\[ Z_H = 0.75 \]
\[ Z_H = 0.75 \]

\[ \text{GaH}_3 \text{As} \text{GaH}_3 \]

\[ \text{m1} \]

\[ \text{m2} \]

\[ \text{m3} \]

\textbf{Figure 2.20:} Model systems for Al\(_x\)Ga\(_{1-x}\)As. The nuclear charges of the pseudo-hydrogen atoms (H and H\(^{'})\) are denoted by \(Z_H\) and \(Z_{H'}\), respectively.

<table>
<thead>
<tr>
<th>(n = 0) and (n = 4)</th>
<th>Sea of Al</th>
<th>Sea of Ga</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\langle \eta \rangle)</td>
<td>0.61</td>
<td>0.61</td>
</tr>
<tr>
<td>(\langle V_{zz} \rangle)</td>
<td>1.19</td>
<td>0.98</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(n = 1) and (n = 3)</th>
<th>Sea of Al</th>
<th>Sea of Ga</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\langle \eta \rangle)</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>(\langle V_{zz} \rangle)</td>
<td>43.6</td>
<td>43.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(n = 2)</th>
<th>Sea of Al</th>
<th>Sea of Ga</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\langle \eta \rangle)</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td>(\langle V_{zz} \rangle)</td>
<td>43.8</td>
<td>43.4</td>
</tr>
</tbody>
</table>

\textbf{Table 2.13:} Comparison of the average values for \(S = 0\) obtained with the “multipole model” based on DFT calculations for Al\(_{255}\)GaAs\(_{256}\) (“sea of Al”) and for AlGa\(_{255}\)As\(_{256}\) (“sea of Ga”). \(V_{zz}\) is in units of \(10^{-20} \text{ V/m}^2\). The Gallium sea returns slightly lower EFG values.

\textbf{2.10.4 Core states: conclusion}

With the calculations on the molecular models we could test the effect of those core states that are too deep be included (i.e. to unfreeze) in the PAW approach. The effects are small. We have to be careful though: Whereas the arsenic \(V_{zz}\) attains values typical for the solid state environment, the asymmetry necessarily present in these molecular models gives rise to much larger Ga and Al \(V_{zz}\) than we observe in the solid state. In the typical solid state environment, these EFGs are one to two orders of magnitude smaller, and are determined by weak long-range effects. Moreover, from the solid state model calculations we know that, e.g, the 2\(p\) electrons in Al can have substantial relative effects: suppressing the 2\(p\) will only marginally change the absolute size of the EFGs, this small change is however more than 50% of the total Al EFG (table 29).

For reasons of computational efficiency (calculations on large cells of up to 512 atoms have to be carried out) we chose to employ standard PAW projector sets, as are supplied with the VASP package. These allow for a kinetic energy cutoff of 300 eV (500 eV for the augmentation grid). So the full Al core is frozen, all Ga electrons below 3\(d\) are frozen and even the 3\(d\) of arsenic remains frozen. For Al we expect large errors. For Ga the situation is much better, but inaccuracies of several 10% are possible. For arsenic the expected inaccuracies are modest, no more than 5% for As sites with
large EFGs. Somewhat larger inaccuracies are expected for As[Al₄] and As[Ga₄] sites.

### 2.10.5 Choice of DFT functional

The choice of DFT functional has a noticeable effect. Using standard LDA (Perdew-Zunger parametrization of the Cerperley Alder correlation energy of the uniform electron gas) or the Perdew-Burke-Ernzerhof (PBE, Ref. [64]) generalized gradient approximation (GGA) gives a difference of 9% for the As $V_{zz}$ (see table 2.9). This is larger than possible systematic errors resulting from neglect of core-relaxation.

Many studies on EFGs in solids have been carried out using the LDA. Very good results can be obtained. Systematic studies of the effect of exchange-correlation functionals on the EFG in solids have, to our knowledge, not been carried out. More accurate studies beyond DFT methods are not available. In this study we use the state-of-the-art PBE functional for our calculations. It gives good agreement with the experiment.

### 2.10.6 Multipole model

Table 2.13 provides info on the effect of using the “Ga in a sea of Al” or the “Al in a sea of Ga” on the As EFGs.

### 2.11 Simpson

The Hahn-echo and QCPMG Simpson scripts are displayed in appendix K.
Chapter 3

Thin film NMR of AlGaAs

3.1 A Stripline $^{75}$As NMR Study of Epitaxial III-V Semiconductor Al$_{0.5}$Ga$_{0.5}$As

3.2 Abstract

We have carried out $^{75}$As Nuclear Magnetic Resonance (NMR) experiments on a single 5 $\mu$m thick epitaxial layer of metal organic chemical vapor deposition (MOCVD) Al$_x$Ga$_{1-x}$As with $x=0.522$ using a novel stripline based NMR setup. Different Arsenic surroundings in the lattice give rise to five As[Al$_n$Ga$_{4-n}$] sites with $(n = 0\ldots4)$. By mounting a thin film of Al$_{0.522}$Ga$_{0.478}$As in a home built NMR probe with rotation stage and stripline detector, we could successfully distinguish different Arsenic nearest neighbors coordinations. Furthermore, we were able to observe various $^{75}$As quadrupolar tensor orientations for each As[Al$_n$Ga$_{4-n}$] coordination which gives us a unique insight into the structure of this material. The individual resonances for each of these coordinations appear to be very broad, as a result of the variation in the local symmetry due to the distribution of Aluminum and Gallium over the lattice. In particular the NMR resonance of one orientation of the As[Al$_2$Ga$_2$] site is strongly broadened. The line widths prove to be larger than predicted on the basis of the (distribution in) quadrupolar interaction parameters obtained in a previous study of powdered Al$_x$Ga$_{1-x}$ As films [P. J. Knijn et al., Phys. Chem. Chem. Phys., 12 (2010) 11517-11535]. In Density Functional Theory (DFT) based calculations these wider distributions in quadrupolar interaction parameters can be explained by local variations in the first coordination sphere of Arsenic which become apparent when the internal structure is relaxed before quantum mechanical calculations of the Electric Field Gradient Tensors (EFGs). A detailed simulation of the NMR line intensities, taking the actual NMR excitation parameters into account prove the absence of any kind of local or long range order in the occupation of the Al/Ga sites in the lattice.

3.3 Introduction

Nuclear magnetic resonance (NMR) is one of the most information-rich spectroscopies with widespread analytical application in chemistry, biology, medicine and materials research[73, 74, 75, 76, 77, 78, 79]. Nevertheless, one avenue where the application of NMR has not yet fully blossomed is the study of functional thin film semiconductor devices. The reason for the limited application of NMR in semiconductor research is amongst others due to the notion that electrons can be a better source of information in semiconductors. Nevertheless, NMR can be an invaluable tool to characterize inorganic semiconductors to get insight in the concentration and mobility of charge carriers, the chemical nature and local structure of dopants and the overall quality of the crystal lattice and/or the existence of stacking faults or dislocations as has recently been reviewed by Yesinowski[80].

Thin epitaxial layers of III-V alloy semiconductors are of principal interest for creating heterojunctions, quantum wells, selected-wavelength Light Emitting Diodes (LEDs) and Laser Diodes (LDs). The development of new or improved devices relies on a detailed knowledge of the structural properties of the materials and its most prominent defects. The characterization of these compounds is crucial in view of a controlled growth of desired semiconductor structures. Moreover, the degree of order-disorder affects many physical and electronic properties, such as, electronic transport, mobility, electro-optical properties etc. It is in this respect that solid-state NMR can play a significant role in the determination of structural characteristics and degree of ordering in the semiconductor material.

AlGaAs is a well-known semiconductor with interesting electronic and photonic properties. Using X-ray measurements[31] and other analytic techniques[26] a random distribution of the Al and Ga cations within the fixed anion fcc lattice structure was found. Considering the limited number of reports[30, 81] on long-range order in AlGaAs thin films as studied by diffraction techniques, whereas specific ordered structures are seen in a number of microscopic observations (such as SEM, TEM)[82], it is interesting to study these materials with a complimentary method such as NMR. Since NMR gives local structural information with the entire sample contributing to the NMR signal the chance of studying minor anomalies in the structure is reduced.

The high quadrupolar moment of $^{75}$As and its strategic position in the AlGaAs lattice makes it a very interesting nucleus to probe the symmetry and ordering of the crystal lattice. Knijn et al. analyzed the cation ordering in crushed Al$_x$Ga$_{1-x}$As thin film on the basis of the size of the $^{75}$As quadrupolar interaction parameters and the shape and width of their distributions combined with the relative spectral intensities of the $^{75}$As resonance lines in NMR powder spectra[83]. Because of the different powder orientations, the sub-spectra arising from different Arsenic coordinations As[Al$_n$Ga$_{4-n}$] with (n = 0...4) partially overlap due to the second order quadrupolar powder broadening inherent to half-integer quadrupolar nuclei such as $^{75}$As with $I = 3/2$. More subtle studies of potential local order in these materials require the possibility to study a single oriented film. NMR spectra of single epitaxially grown oriented films are similar to single crystal spectra giving resonances of the various inequivalent sites in the unit cell. If dipolar interactions are minor, the lines will be narrow and eventual line broadening can be interpreted in terms of local order or disorder that may be present in these thin films. This is a great advantage over powder spectra where this information is convoluted with the orientation distribution of individual powder particles (the
second-order powder pattern). In the $^{75}\text{As}$ spectra of AlGaAs, the various arsenic resonances can be related to distinct $^{75}\text{As}$ Electric Field Gradient (EFG) tensor orientations of the different As coordinations based on their first shell configurations.

In this contribution, we study a thin film of Al$_x$Ga$_{1-x}$As with $x = 0.522$ using a home-built stripline-based NMR probe. Compared to the powder micro-coil setup\cite{83}, the stripline\cite{84} configuration has several advantages. In a stripline the current is fed through a thin metal strip which is placed at some distance above a metal ground plane. A non-radiative closed configuration is realized by placing ground planes both above and below the strip. The magnetic field lines encircle the central strip, so the $B_1$ field points in opposite directions above and below the stripline. The boundary conditions at the metal surface dictate that the field lines run parallel to this surface and as a result the $B_1$ field homogeneity is quite good. High in-plane "surface" sensitivity is generated, which is ideally suitable for studying thin films. Attractive points of the stripline are the fact that the sensitivity is competitive with optimized helical coils where the effective filling factor is a major issue when studying thin films. Furthermore, it is possible to rotate the thin film sample on top of the stripline which is used to generate characteristic rotation patterns of various sites in the material.

The main challenge of this study is the very poor signal-to-noise (S/N) ratio of $^{75}\text{As}$ NMR spectra of the AlGaAs thin film. This is mainly due to the almost prohibitively small sample volume of maximally 70 nL (the thickness of the thin film is 5 $\mu$m and the area above the resonant part of the stripline was $2\text{mm} \times 7\text{mm}$), combined with low reactivity of $^{75}\text{As}$ (0.0254 relative to $^1\text{H}$). A 70 nL sample contains about $\sim 4 \times 10^{17}$ As spins which is at the theoretical detection limit of conventional NMR set-ups ($\sim 10^{16}$-$10^{18}$ (high gamma) spins\cite{85, 86, 87}). This is further complicated by the fact that the resonances are distributed over a spectral range of several MHz due to the large quadrupolar coupling.

Here we present resolved spectra of $^{75}\text{As}$ in a single Al$_x$Ga$_{1-x}$As ($x = 0.522$) thin film. In the spectra, we can clearly distinguish the different $^{75}\text{As}$ coordinations As[Al$_n$Ga$_{4-n}$] with ($n = 0..4$) indicating the number of Al and Ga in the first coordination sphere. The direct observation of the $^{75}\text{As}$ EFG tensor orientations within each coordination provides us with a unique insight into the structure of the material. The resonance assignments can be done by rotating the thin film sample on top of the stripline and comparing their resonance positions with the simulated rotation pattern based on the quadrupolar parameters determined by Knijn et al\cite{83}. The measurements are very time consuming and therefore only parts of the rotation pattern could be acquired within reasonable measurement time. We show by using Density Functional Theory (DFT) quantum mechanical calculations that the experimental NMR line widths can be explained by local structural variations within the AlGaAs thin film due to the distribution of Al and Ga over the lattice.

### 3.4 Experimental

#### 3.4.1 Sample Preparation

The Al$_x$Ga$_{1-x}$As sample was grown by Metal Organic Chemical Vapor Deposition. An undoped 2 inch GaAs wafer with crystal surface orientation (001) was used as substrate. The layer structure consisted of a GaAs buffer layer followed by a 30 nm thick InGaP etch stop layer and the 5 $\mu$m
\( \text{Al}_x \text{Ga}_{1-x} \text{As} \) top layer. The pressure and temperature during growth were 20 mbar and 700 °C. For the AlGaAs layer AsH3, TMAI (trimethylaluminium) and TMGa were used as source materials at a V/III ratio of 125. Under these growth conditions and due to the very small lattice mismatch between substrate and epilayer the AlGaAs obtained is single crystalline and of high quality. In the next step the 350 \( \mu \text{m} \) GaAs wafer was removed by a wet chemical etch process. For this purpose the epilayer side of the sample was glued to a supporting plastic foil with a thickness of 250 \( \mu \text{m} \) to allow back side etching with a citric acid - hydrogen peroxide solution (5 : 1). After about 24 hours the etch process stops at the InGaP layer which is subsequently removed in a HCl solution leaving an AlGaAs thin film on the plastic foil.

### 3.4.2 XRD Experiments

A high resolution X-ray diffraction rocking curve of the (004) reflection was measured with the \( \text{Al}_x \text{Ga}_{1-x} \text{As} \) layer still on the wafer to determine the stoichiometry. From the distance between the GaAs substrate and the \( \text{Al}_x \text{Ga}_{1-x} \text{As} \) epilayer diffraction peaks a value of 0.522 was calculated for \( x \), which is close to the intended 0.5. The thin film was grown on a (001) surface plane in the (100) direction. Using XRD data we could also identify the (100) crystal plane on the wafer. In this way the crystal x-axis (pointing towards (100) plane), and z-axis (pointing towards (001) plane) were defined. This information is used to define the Euler angles \( \alpha_{\text{CL}} \), and \( \beta_{\text{CL}} \) orienting the thin film with respect to the external \( \text{B}_0 \) field in the NMR experiments.

### 3.4.3 NMR Experiments

A static stripline probe was designed and used to record the \( ^{75} \text{As} \) spectra. The home-built stripline probe is displayed in Fig 3.1. In this design the basic element is the stripline radio frequency, RF 'coil'. The structure is machined in Rogers RT/durroid 5870 PTFE (Polytetrafluoroethylene) based high frequency laminate board and is adapted to the dimensions of the sample. The stripline structure is embedded between equally spaced ground planes and is connected to one of the ground planes on one end.

The stripline is inserted as a short at one side of a \( \lambda/4 \) free space coaxial resonator and capacitively coupled and matched to the 50Ω circuit. The position of the matching is relatively close to the shorted end of the coaxial resonator where the line voltage is still relatively low to avoid arcing. The matching takes place inside the \( \lambda/4 \) resonator, by insertion of a PTFE stub inside a short copper tube which is capacitively coupled to the inner conductor of the coaxial resonator. The tuning is realized by the insertion of a PTFE stub at the open end of the coaxial resonator thus changing the physical length of the standing wave in the coaxial line. The width of the stripline is 2 mm and the length 7 mm. The Q-factor of the probe is 212.

The experiments were performed on a Varian NMR System (VNMRS) 850 MHz (19.96 T) spectrometer. Hahn-Echo[8] experiments were performed observing the spin-3/2 \( ^{75} \text{As} \) resonance (145.542 MHz) in the \( \text{Al}_0.522 \text{Ga}_{0.478} \text{As} \) sample. Based on the quadrupolar interaction parameters from the powder study[83], the frequency range of the central transitions of the \( n = 1, 2, \) and 3 sites was estimated to run from \( \sim -1.2 \) to 0.65 MHz. Instead of a single echo at the center frequency,
we performed frequency-stepped Hahn-Echo experiments\cite{74, 88, 89} covering a region between -1.25 MHz to 1.0 MHz in steps of \( \sim 100 \) kHz. At each step the probe was retuned. The spectra were then added to get a complete \(^{75}\)As spectrum. A recycle delay of 2 s was employed. Whole echoes were recorded which were processed by swapping the data around the echo maximum. This was followed by apodization (exponential) and zero-filling to 16384 points before Fourier transformation. All data processing was done using the matNMR software\cite{90}. The spectral width was 2.5 MHz at each step. The Hahn-Echo spectra were acquired with echo times of \( \tau_1 = 50 \) \( \mu \)s and \( \tau_2 = 30 \) \( \mu \)s. The RF amplitude of the excitation and refocussing pulses was 111 kHz at a power of 670 Watt. The RF power calibration was performed using a \( \sim 300 \) \( \mu \)m thick GaAs sample, where As is in a symmetric coordination without quadrupolar broadening.

The RF pulse width used for the excitation pulse was 1.1 \( \mu \)s corresponding to a \( \pi/2 \) pulse assuming selective excitation of the central -1/2 = +1/2 transition. To achieve uniform excitation of all the different quadrupolar sites this short pulse was applied on resonance for each sites in the frequency-stepped experiments. This condition was maintained to ensure selective excitation of the central transition for all sites except the symmetric the As[Ga₄] and As[Al₄] resonances which have
much smaller quadrupolar interactions. Simulations were carried out using the SIMPSON simulation program (version 3.0.1)\cite{59}. The Hahn-echo response of each quadrupolar tensor orientation was simulated using the experimental pulse sequence that included all pulses, timings and field strengths as executed in the experiments.

3.5 Theory

3.5.1 EFG tensor orientations

We define the Principle Axes Frame (PAF) of the EFG tensor as our starting frame. The Euler angles ($\alpha_{PC}, \beta_{PC}, \gamma_{PC}$) relate the principle axes frame (PAF) of the EFG tensor ($V_{XX}, V_{YY}, V_{ZZ}$) to the crystal frame ($V_{X'X'}, V_{Y'Y'}, V_{Z'Z'}$) defined by the unit cell orientation as determined by the XRD experiments (Fig 2). We use the convention of rotations as described by Levitt\cite{4}.

Based on the first shell Arsenic coordination, five different sites As[Al$_n$Ga$_{4-n}$] with ($n=0...4$) can be distinguished within an AlGaAs single crystal. Due to the symmetry of the As[Ga$_4$] and As[Al$_4$] sites, they in principle should not experience any electric field gradient and therefore the quadrupolar interaction should be zero. However, considering the contributions from the third and higher shells, these sites do experience a non-zero quadrupolar interaction. With a random long range cation distribution, the tensor orientations of these sites become equally distributed over all possible directions\cite{83} in which case the resonances from these sites will be position invariant. Inspection of the positions of the As[Ga$_4$] and As[Al$_4$] resonances as a function of orientation will therefore give a first insight into the randomness of the distribution of Al and Ga over the lattice. The size of the EFG tensor for the $n=1,2,3$ sites is mostly determined by their first shell coordination, and each of these sites can occur in a number ($\leq 3$) of discrete orientations in the single crystal. Fig. 3.3 shows all the possible orientations for the $n=1,2,3$ coordinations. For each coordination the orientation of the main principle value $V_{ZZ}$ of the EFG tensors is shown as well. All possible, discrete Euler angles of the $V_{ZZ}$ vectors which transform them from PAF to crystal frames were determined from the first shell geometry in the lattice. There are total 12 possible orientations of $V_{ZZ}$ vector for As[Al$_2$Ga$_2$] coordination and 8 possible orientations for As[Al$_{1/3}$Ga$_{3/1}$] (Table 3.1).

However, because of the symmetry of the EFG tensors out of 12 possible orientations for As[Al$_2$Ga$_2$] coordination only 6 are distinguishable (Figs. 3.3(a), (b), and (c)). In this particular case with $\eta = 1$ the number of distinguishable orientations reduces to 3 as $|V_{XX}| = |V_{ZZ}|$. For As[Al$_{1/3}$Ga$_{3/1}$], out of 8 possible orientations 4 are distinguishable (Figs. 3.3(d) and (e)) which reduces to 2 because of the cylindrical symmetry ($\eta = 0$, $V_{XX} = V_{YY}$). Hence in total we expect seven NMR lines, 2 from the symmetric sites with $n=0$ and 4 respectively. We expect 3 lines for sites with $n=2$ and 2 more NMR lines for sites with $n=1,3$.

3.5.2 Computational modeling

Electric field gradients (EFG) have been calculated from first-principles with the Vienna ab initio simulation package\cite{32,53}. The EFG were obtained with the projector augmented wave (PAW) method\cite{61,62} following\cite{91}. Technical details are similar to the study on powdered AlGaAs films
Figure 3.2: Schematic representation of the Euler angles used to transform the EFG tensor from the Principle Axis Frame (PAF) to the Crystal Frame (CF), using the $z$-$y$-$z$ convention. $V_{XX}$, $V_{YY}$, and $V_{ZZ}$ represent the principle values of the EFG tensor in PAF and $V'_{XX}$, $V'_{YY}$, and $V'_{ZZ}'$ are the principle values of the EFG tensor in the crystal frame.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Coordination Site</th>
<th>EFG Tensor orientations</th>
</tr>
</thead>
</table>
| Al$_x$Ga$_{1-x}$As thin film | As[Al$_2$Ga$_2$]   | $\alpha_{PC}=0^\circ$, $\beta_{PC} =45^\circ$  
$\alpha_{PC}=0^\circ$, $\beta_{PC} =135^\circ$  
$\alpha_{PC}=180^\circ$, $\beta_{PC} =45^\circ$  
$\alpha_{PC}=180^\circ$, $\beta_{PC} =135^\circ$  
$\alpha_{PC}=90^\circ$, $\beta_{PC} =135^\circ$  
$\alpha_{PC}=90^\circ$, $\beta_{PC} =45^\circ$  
$\alpha_{PC}=270^\circ$, $\beta_{PC} =135^\circ$  
$\alpha_{PC}=270^\circ$, $\beta_{PC} =45^\circ$  
$\alpha_{PC}=45^\circ$, $\beta_{PC} =90^\circ$  
$\alpha_{PC}=135^\circ$, $\beta_{PC} =90^\circ$  
$\alpha_{PC}=315^\circ$, $\beta_{PC} =90^\circ$  
$\alpha_{PC}=225^\circ$, $\beta_{PC} =90^\circ$ |
| As[Al$_{3/1}$Ga$_{1/3}$] |                   | $\alpha_{PC}=45^\circ$, $\beta_{PC} =125.3^\circ$  
$\alpha_{PC}=135^\circ$, $\beta_{PC} =125.3^\circ$  
$\alpha_{PC}=315^\circ$, $\beta_{PC} =125.3^\circ$  
$\alpha_{PC}=225^\circ$, $\beta_{PC} =125.3^\circ$  
$\alpha_{PC}=135^\circ$, $\beta_{PC} =54.7^\circ$  
$\alpha_{PC}=45^\circ$, $\beta_{PC} =54.7^\circ$  
$\alpha_{PC}=315^\circ$, $\beta_{PC} =54.7^\circ$  
$\alpha_{PC}=225^\circ$, $\beta_{PC} =54.7^\circ$ |

Table 3.1: All possible, discrete Euler angles of the $V_{ZZ}$ vectors which transform EFG tensor from PAF to Crystal frames for As[Al$_2$Ga$_2$] coordination and As[Al$_{3/1}$Ga$_{1/3}$] coordination.
Figure 3.3: The first shell Arsenic surroundings for As[AlₙGa₄₋ₙ] where n = 1, 2, 3 in AlGaAs thin film. The blue arrows show the direction of the Vzz direction of the ⁷⁵As EFG tensors. (a), (b), and (c) show the pairs of Vzz orientations for As[Al₂Ga₂] coordination site. (d) and (e) show the orientations of pairs of Vzz vectors in As[Al₃/₁Ga₁/₃] coordination sites. Because of symmetry considerations the upper and lower orientations produce identical NMR rotational patterns (see text). (a) top: αₚₑₗ = 0° and βₚₑₗ = 45°, bottom: αₚₑₗ = 0° and βₚₑₗ = 135°, (b) top: αₚₑₗ = 90° and βₚₑₗ = 45°, bottom: αₚₑₗ = 90° and βₚₑₗ = 135°, (c) top: αₚₑₗ = 45°, and βₚₑₗ = 90°, bottom: αₚₑₗ = 90°, and βₚₑₗ = 90°, (d) top: αₚₑₗ = 135°, and βₚₑₗ = 54.7°, bottom: αₚₑₗ = 45°, βₚₑₗ = 54.7°, (e) top: αₚₑₗ = 225°, and βₚₑₗ = 125.3°, bottom: αₚₑₗ = 135°, and βₚₑₗ = 125.3°.
3.5. THEORY

<table>
<thead>
<tr>
<th>Sample</th>
<th>Coordination Site</th>
<th>EFG Tensor orientations</th>
<th>(\eta_Q)</th>
<th>(C_Q/\text{MHz})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Al}<em>{0.522}\text{Ga}</em>{0.478}\text{As}) thin film</td>
<td>As[Al(_2)Ga(_2)]</td>
<td>(\alpha_{PC}=0^\circ), (\beta_{PC}=45^\circ)</td>
<td>0.90±0.06</td>
<td>32.7±0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\alpha_{PC}=45^\circ), (\beta_{PC}=90^\circ)</td>
<td>0.98±0.02</td>
<td>33.0±0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\alpha_{PC}=90^\circ), (\beta_{PC}=45^\circ)</td>
<td>0.97±0.02</td>
<td>33.0±0.3</td>
</tr>
<tr>
<td>(\text{Al}<em>{0.489}\text{Ga}</em>{0.511}\text{As}) powder</td>
<td>As[Al(_2)Ga(_2)]</td>
<td>-</td>
<td>0.98</td>
<td>30.5±0.1</td>
</tr>
<tr>
<td></td>
<td>As[Al(_{3}/2)Ga(_1/3)]</td>
<td>-</td>
<td>0.03</td>
<td>33.3±0.1</td>
</tr>
</tbody>
</table>

Table 3.2: The \(^{75}\text{As}\) quadrupolar parameters of various sites obtained from the 1D Hahn-Echo experiments in \(\text{Al}_{0.522}\text{Ga}_{0.478}\text{As}\) thin film compared with the powder data in Ref. [83]. The quadrupolar parameters were estimated from the resonance positions of various sites at different \(\alpha_{CL}\).

<table>
<thead>
<tr>
<th>(a) (Å)</th>
<th>(\text{no relaxation})</th>
<th>(\text{relaxations})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{As[AlGa}_4\text{]})</td>
<td>0.80 (0.22)</td>
<td>1.04 (0.26)</td>
</tr>
<tr>
<td>(\text{As[Al}_1\text{Ga}_3\text{]})</td>
<td>32.91 (0.61)</td>
<td>32.07 (0.74)</td>
</tr>
<tr>
<td>(\text{As[Al}_2\text{Ga}_2\text{]})</td>
<td>33.24 (0.62)</td>
<td>32.27 (0.76)</td>
</tr>
<tr>
<td>(\text{As[Al}_3\text{Ga}_1\text{]})</td>
<td>32.50 (0.49)</td>
<td>31.51 (0.59)</td>
</tr>
<tr>
<td>(\text{As[Al}_4\text{Ga}\text{]})</td>
<td>1.13 (0.32)</td>
<td>1.37 (0.38)</td>
</tr>
</tbody>
</table>

Table 3.3: Average \(^{75}\text{As}\) \(C_Q\) (MHz) for various cationic occupancies of the first neighbor shell calculated without (Ref [83]) and with structural relaxation (this study). Root-mean-square deviations from the average are between brackets.

by Knijn et al.[83] with the exception that in this study structural relaxations are implemented which were deemed unnecessary in the powder study (vide infra). As a starting point we took the "supercell models"[83] taking 10 configurations with composition \(\text{Al}_{16}\text{Ga}_{16}\text{As}_{32}\), with \(\text{Al}\) and \(\text{Ga}\) cations randomly distributed over the cationic sites of an ideal Zincblende lattice (Order parameter \(S \approx 0\)), in periodically repeated cubic boxes. The order parameter \(S\) is defined to quantify the degree of long-range order related to the fractional occupancy of lattice sites by their preferred atoms[30]: \(S = 0\) represents a completely random structure and \(S = 1\) corresponds to a completely ordered lattice. We fixed the lattice parameter to \(a = 2 \times 5.66544\) Å, i.e. twice the average of the experimental GaAs and AlAs lattice constants, so just the sum = 11.3309 and relaxed the structure with the model pair potential. This approach yields a bond length of either \(5.66140\) Å or \(5.66949\) Å, depending on the cationic species of the bond (i.e. GaAs and AlAs bonds respectively).
Figure 3.4: Experimental summed 1D Hahn-Echo spectrum of $^{75}$As nuclei in Al$_{0.522}$Ga$_{0.478}$As thin film obtained on a VNMRS 850 spectrometer at different $\alpha_{CL}$ angles, (a) $\alpha_{CL} = 0^\circ$ (number of scans = 82000), (b) $\alpha_{CL} = 30^\circ$ (number of scans = 82000), (c) $\alpha_{CL} = 60^\circ$ (number of scans = 128000), and (d) $\alpha_{CL} = 90^\circ$ (number of scans = 156000). At the right hand side of each spectrum a schematic representation of the orientation of the thin film on top of the stripline with respect external magnetic field $B_0$ is given. The orientations of the lattice vectors with respect to the thin film are indicated in the top figure. For $\alpha_{CL} = 0^\circ$, the lattice vector $a$ is aligned with the external magnetic field $B_0$. 
Figure 3.5: (a) Experimental NMR resonance positions and numerically simulated rotation patterns of the various $^{75}$As NMR resonances in Al$_{0.522}$Ga$_{0.478}$As thin film, based on the average quadrupolar interaction parameters obtained from the powder study and the orientation of the film as determined by X-Ray diffraction. (b) Theoretically predicted rotation patterns of various sites generated using the EFG parameters estimated from DFT quantum mechanical calculations. The width of each line represent the theoretically predicted line widths of the NMR resonances resulting from the distributions in their EFG parameters due to the positional disorder of Al and Ga in the lattice.
3.5.3 Rotation Pattern

The quadrupolar Hamiltonian, $H_Q$, besides generally being larger than the other internal spin Hamiltonians, often dominates over the typical radiofrequency (rf) fields employed in NMR. For an analysis of quadrupolar spectra, the first two terms in the Magnus expansion[92] are considered. The quadrupolar interaction shifts the eigenvalues of the Zeeman Hamiltonian, resulting in an NMR spectrum that is split into (2I+1) peaks. The first-order quadrupolar interaction, $H^{(1)}_Q$ affects only the satellite transitions $m \leftrightarrow m+1$, where $|m|$ takes the values $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$. As a result, the observable satellite transitions are spread over a large bandwidth (up to tens of MHz) and therefore they often escape detection. However, the symmetric transitions $-m \leftrightarrow +m$ are affected by the relatively smaller second-order quadrupolar interaction, $H^{(2)}_Q$, only. Hence, the observable single-quantum transition of half-integer quadrupolar spins, $-\frac{1}{2} \leftrightarrow +\frac{1}{2}$, called the central transition (CT), displays a relatively narrow spread of resonance frequencies and as a result are much easier to observe.

Because of the magnitude of the quadrupolar interaction which is associated with $^{75}$As in Al$_x$Ga$_{1-x}$As, we may assume that the $^{75}$As central transition (CT) NMR spectrum is dominated by the $H^{(2)}_Q$. The chemical shift range for $^{75}$As nuclei is $\sim 600$ ppm, which though appreciable ($\sim 0.09$ MHz) at high magnetic field, is still much less than the total possible dispersion of CT resonances ($\sim 2.1$ MHz) due to the second order quadrupolar interaction at 19.96 T. The heteronuclear dipolar couplings between $^{75}$As - $^{69/71}$Ga ranges between 350 to 450 Hz and that between $^{75}$As - $^{27}$Al is $\sim 370$ Hz (estimated from the bond distances given in Fig. 1 of Ref. [42]). The homonuclear dipolar coupling between $^{75}$As - $^{75}$As is even less ($\sim 50$ Hz) [42]. Hence we can safely assume that the $^{75}$As CT resonance positions for different sites in Al$_x$Ga$_{1-x}$As will be determined predominantly by second-order quadrupolar interaction, $H^{(2)}_Q$ as was confirmed in the powder study. The Euler angles that relate the PAF of the EFG tensor to the crystal frame ($\alpha_{PC}, \beta_{PC}$ and $\gamma_{PC}$) and the relative orientation of the crystal (epitaxial thin film) with respect to the B$_0$ field ($\alpha_{CL}, \beta_{CL}$ and $\gamma_{CL}$) determine the resonance frequency of each site. The angular dependency of the satellite and central transitions is derived from the Hamiltonian in the laboratory (LAB) frame, written in spherical tensor components. A transformation from the Principle Axis Frame (PAF) to the crystal frame (CRY), to the LAB frame can be done by applying two consecutive Wigner rotations[5, 6].

$$PAF^{\alpha_{PC},\beta_{PC},\gamma_{PC}} \rightarrow CRY^{\alpha_{CL},\beta_{CL},\gamma_{CL}} \rightarrow LAB.$$  

Here, $\beta_{CL}$ is set to 90° accounting for the orientation of the stripline and thus the thin film with respect to the external B$_0$ field, with the z-axis of the crystal frame being perpendicular to the field.

The Hamiltonian for the second order quadrupolar interaction can be written as derived from the Magnus expansion[92],

$$H^{(2)}_Q = \frac{(eQ)^2}{\omega_0(2I(2I-1))^2} \cdot \left\{ \frac{1}{2}V_{2,-1}V_{2,1}(4I(I+1) - 8I_z^2 - 1) \\
+ \frac{1}{2}V_{2,-2}V_{2,2}(2I(I+1) - 2I_z^2 - 1) \right\} I_z$$

with $V_{2,i}$ being the irreducible spherical tensor representation of the EFG.
3.5. **THEORY**

A product of two second rank tensors can be written as a sum of tensors with rank up to \(2 + 2 = 4\).

\[
V_{2,-1}V_{2,1} = \sqrt{\frac{8}{35}}W_{4,0} + \sqrt{\frac{1}{14}}W_{2,0} - \sqrt{\frac{1}{5}}W_{0,0}
\]

\[
V_{2,-2}V_{2,2} = \sqrt{\frac{1}{70}}W_{4,0} + \sqrt{\frac{2}{7}}W_{2,0} + \sqrt{\frac{1}{5}}W_{0,0}
\]

so that \(H_Q^{(2)}\) can be re-written as

\[
H_Q^{(2)} = - \frac{(eQ)^2}{\omega_0(2I(2I-1))^2} \cdot \left( \frac{\sqrt{70}}{140} W_{4,0} (18I(I+1) - 35I_z^2 - 5) + \frac{\sqrt{11}}{28} W_{2,0} (8I(I+1) - 12I_z^2 - 3) - \frac{1}{\sqrt{5}} W_{0,0} (I(I+1) - 3I_z^2) \right) I_z
\]

and the central transition resonance frequency becomes,

\[
\omega_{1/2,-1/2}^{(2)} = - \frac{(eQ)^2}{\omega_0(2I(2I-1))^2} \cdot \left( \frac{1}{\sqrt{70}} W_{4,0} (9I(I+1) - 7/4) + \frac{1}{\sqrt{14}} W_{2,0} (4I(I+1) - 3) - \frac{1}{\sqrt{5}} W_{0,0} (I(I+1) - 3/4) \right)
\]

Using the EFG parameters obtained from the DFT calculations we calculated the values of \(W_{0,0}^{LAB}\), \(W_{2,0}^{LAB}\) and \(W_{4,0}^{LAB}\) (see Appendix) for all the possible quadrupolar tensor orientations within \(\text{Al}_2\text{Ga}_{1-x}\text{As}\). From these values we can predict the central transition (CT) resonance positions for each of the possible tensor orientations at angles \(0^\circ \leq \alpha_{CL} \leq 90^\circ\) describing the rotation of the thin film. We also calculated the distributions in CT resonance positions for each set of the tensor orientations caused by the variations in their EFG parameters and Euler angles, \(\alpha_{PC}, \beta_{PC}\) and \(\gamma_{PC}\) due to the random distributions of Al and Ga over the lattice \((S = 0)\) combined with the effects of structural relaxation of the \(\text{AlGaAs}\) structure. These values were obtained from the DFT quantum mechanical calculations. This procedure was used to validate the DFT calculations with respect to the experimental results. We furthermore used the numerical simulation program SIMPSON to calculate the CT line positions and intensities at various \(\alpha_{CL}\) angles in order to reproduce the experimental CT resonance positions (using the experimentally determined rf-field strength) for each of the \(^{75}\text{As}\) NMR resonances in \(\text{AlGaAs}\) thin film and extract their quadrupolar parameters and relative intensities.

Because of the magnitude of the quadrupolar interaction which is associated with \(^{75}\text{As}\) in \(\text{Al}_2\text{Ga}_{1-x}\text{As}\), we may assume that the \(^{75}\text{As}\) central transition (CT) NMR spectrum is dominated by the \(H_Q^{(2)}\). The chemical shift range for \(^{75}\text{As}\) nuclei is \(\sim 600\) ppm, which though appreciable at high magnetic field, is still much less than the total possible dispersion of CT resonances (\(\sim 2.1\) MHz) due to the second order quadrupolar interaction at 19.96 T. The heteronuclear dipolar couplings between \(^{75}\text{As} - ^{69/71}\text{Ga}\) ranges between 350 to 450 Hz and that between \(^{75}\text{As} - ^{27}\text{Al}\) is \(\sim 370\) Hz.
<table>
<thead>
<tr>
<th>Procedure</th>
<th>Coordination Site</th>
<th>EFG Tensor orientations</th>
<th>linewidth / kHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>As[Al₂Ga₂]</td>
<td>$\alpha_{PC} = 0^\circ, \beta_{PC} = 45^\circ$</td>
<td>250±20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha_{PC} = 45^\circ, \beta_{PC} = 90^\circ$</td>
<td>60±5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha_{PC} = 90^\circ, \beta_{PC} = 45^\circ$</td>
<td>49±6</td>
</tr>
<tr>
<td></td>
<td>As[Al₃/₁Ga₁/₃]</td>
<td>$\alpha_{PC} = 135^\circ, \beta_{PC} = 125.3^\circ$</td>
<td>51±3*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha_{PC} = 135^\circ, \beta_{PC} = 54.7^\circ$</td>
<td>51±3*</td>
</tr>
<tr>
<td>Theoretical</td>
<td>As[Al₂Ga₂]</td>
<td>$\alpha_{PC} = 0^\circ, \beta_{PC} = 45^\circ$</td>
<td>170 [77.7]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha_{PC} = 45^\circ, \beta_{PC} = 90^\circ$</td>
<td>40.45 [23.37]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha_{PC} = 90^\circ, \beta_{PC} = 45^\circ$</td>
<td>34.8 [19.53]</td>
</tr>
<tr>
<td></td>
<td>As[Al₃/₁Ga₁/₃]</td>
<td>$\alpha_{PC} = 135^\circ, \beta_{PC} = 125.3^\circ$</td>
<td>37.3 [17.33]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha_{PC} = 135^\circ, \beta_{PC} = 54.7^\circ$</td>
<td>36.9 [16.98]</td>
</tr>
</tbody>
</table>

**Table 3.4:** Comparison of $^{75}$As NMR linewidths obtained experimentally and theoretically (DFT calculation) for Al₀.₅₂₂Ga₀.₄₇₈As thin film at $\alpha_{CL} = 0^\circ$. Theoretical linewidths resulting from the DFT calculations without structural relaxation are given in parenthesis.

<table>
<thead>
<tr>
<th>Site</th>
<th>$p_{1}$ ($S = 0$)</th>
<th>$I_{1a}$ (Simulated)</th>
<th>$I_{1a}$ (Exp. Thin Film)</th>
<th>$I_{1a}$ (Exp. Powder)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As[Ga₄]</td>
<td>0.05</td>
<td>0.08</td>
<td>0.075±0.025</td>
<td>0.089</td>
</tr>
<tr>
<td>As[Al₁Ga₃] + As[Al₃Ga₁]</td>
<td>0.5</td>
<td>0.431</td>
<td>0.45±0.07</td>
<td>0.43</td>
</tr>
<tr>
<td>As[Al₂Ga₂]</td>
<td>0.37</td>
<td>0.395</td>
<td>0.40±0.07</td>
<td>0.42</td>
</tr>
<tr>
<td>As[Al₄]</td>
<td>0.07</td>
<td>0.093</td>
<td>0.09±0.02</td>
<td>0.065</td>
</tr>
</tbody>
</table>

**Table 3.5:** Comparison of the relative $^{75}$As NMR line intensities. The first column shows the probabilities $p_{1}$ based on the order parameter model assuming $S = 0$. The second column displays the relative intensities obtained using numerical SIMPSON simulations assuming $S = 0$ (i.e. the probabilities in the first column) and taking the exact experimental conditions into account. The third and fourth column give the experimental $^{75}$As NMR line intensities for Al₀.₅₂₂Ga₀.₄₇₈As thin film and powder respectively.
Figure 3.6: (a) The theoretical relative occurrence $p_n$ of the As[Al$_x$Ga$_{1-x}$] sites as a function of the CuPt order parameter $S$ in Al$_x$Ga$_{1-x}$As for $x = 0.522$. The experimental relative intensities based on a direct integration of the resonances are plotted as horizontal lines where the widths of the lines represent the confidence limits, (b) The theoretical relative occurrence $p_n$ as a function of the CuAu order parameter $S$ for $x = 0.522$. The experimental relative intensities are again plotted as horizontal lines where the widths of the lines represent the confidence limits. The simulated relative intensities taking the exact experimental conditions into account are shown as diamonds (◊).
(estimated from the bond distances given in Fig. 1 of Ref. [42]). The homonuclear dipolar coupling between $^{75}$As - $^{75}$As is even less ($\sim 50$ Hz) [42]. Hence we can safely assume that the $^{75}$As CT resonance positions for different sites in Al$_x$Ga$_{1-x}$As will be determined predominantly by second-order quadrupolar interaction, $H_Q^{(2)}$ as was confirmed in the powder study. The Euler angles that relate the PAF of the EFG tensor to the crystal frame ($\alpha_{PC}$, $\beta_{PC}$ and $\gamma_{PC}$) and the relative orientation of the crystal (epitaxial thin film) with respect to the $B_0$ field ($\alpha_{CL}$, $\beta_{CL}$ and $\gamma_{CL}$) determine the resonance frequency of each site. The angular dependency of the satellite and central transitions is derived from the Hamiltonian in the laboratory (LAB) frame, written in spherical tensor components. A transformation from the Principle Axis Frame (PAF) to the crystal frame (CRY), to the LAB frame can be done by applying two consecutive Wigner rotations[5, 6].

$$PAF^{\alpha_{PC},\beta_{PC},\gamma_{PC}} \rightarrow CRY^{\alpha_{CL},\beta_{CL},\gamma_{CL}} \rightarrow LAB.$$  

Here, $\beta_{CL}$ is set to $90^\circ$ accounting for the orientation of the stripline and thus the thin film with respect to the external B$_0$ field, with the $z$-axis of the crystal frame being perpendicular to the field.

The Hamiltonian for the second order quadrupolar interaction can be written as derived from the Magnus expansion [92],

$$H_Q^{(2)} = \frac{(eQ)^2}{\omega_0 (2I(2I-1))^2} \cdot \frac{1}{2} V_{2,-1} V_{2,1} (4I(I+1) - 8I_z^2 - 1) + \frac{1}{2} V_{2,-2} V_{2,2} (2I(I+1) - 2I_z^2 - 1) I_z$$

with $V_{2,i}$ being the irreducible spherical tensor representation of the EFG.

A product of two second rank tensors can be written as a sum of tensors with rank up to $2 + 2 = 4$.

$$V_{2,-1} V_{2,1} = \sqrt{\frac{8}{35}} W_{4,0} + \sqrt{\frac{1}{14}} W_{2,0} - \sqrt{\frac{1}{5}} W_{0,0}$$

$$V_{2,-2} V_{2,2} = \sqrt{\frac{1}{70}} W_{4,0} + \sqrt{\frac{2}{7}} W_{2,0} + \sqrt{\frac{1}{5}} W_{0,0}$$

so that $H_Q^2$ can be re-written as

$$H_Q^{(2)} = -\frac{(eQ)^2}{\omega_0 (2I(2I-1))^2} \cdot \left\{ \frac{\sqrt{70}}{140} W_{4,0} \left( 18I(I+1) - 35I_z^2 - 5 \right) + \frac{\sqrt{14}}{28} W_{2,0} \left( 8I(I+1) - 12I_z^2 - 3 \right) - \frac{1}{\sqrt{5}} W_{0,0} \left( I(I+1) - 3I_z^2 \right) \right\} I_z$$

and the central transition resonance frequency becomes,

$$\omega_{1/2, -1/2}^{(2)} = -\frac{(eQ)^2}{\omega_0 (2I(2I-1))^2} \cdot \left\{ \frac{1}{\sqrt{70}} W_{4,0} \left( 9I(I+1) - 7/4 \right) + \frac{1}{\sqrt{14}} W_{2,0} \left( 4I(I+1) - 3 \right) - \frac{1}{\sqrt{5}} W_{0,0} \left( I(I+1) - 3/4 \right) \right\}.$$
3.6. RESULTS AND DISCUSSION

Using the EFG parameters obtained from the DFT calculations we calculated the values of $W_{0,0}^{LAB}$, $W_{2,0}^{LAB}$ and $W_{4,0}^{LAB}$ (see Appendix) for all the possible quadrupolar tensor orientations within $\text{Al}_x\text{Ga}_{1-x}\text{As}$. From these values we can predict the central transition (CT) resonance positions for each of the possible tensor orientations at angles $0^\circ \leq \alpha_{CL} \leq 90^\circ$ describing the rotation of the thin film. We also calculated the distributions in CT resonance positions for each set of the tensor orientations caused by the variations in their EFG parameters and Euler angles, $\alpha_{PC}$, $\beta_{PC}$ and $\gamma_{PC}$ due to the random distributions of Al and Ga over the lattice combined with the effects of structural relaxation of the AlGaAs structure. These values were obtained from the DFT quantum mechanical calculations. We furthermore used the numerical simulation program SIMPSON to predict the CT line positions and intensities at various $\alpha_{CL}$ angles based on the quadrupolar parameters as obtained from the experimental CT resonance positions (and the experimentally determined rf-field strength) and thus generated the rotation patterns for each of the $^{75}\text{As}$ NMR resonances in AlGaAs thin film as a function of $\alpha_{CL}$.

3.6 Results and Discussion

Fig. 3.4(a) displays the summation of the experimental $^{75}\text{As}$ Hahn-Echo sub-spectra for each frequency offset for $\text{Al}_{0.522}\text{Ga}_{0.478}\text{As}$ at $\alpha_{CL} = 0^\circ$. Contrary to the powder spectrum showing five resonances[83], in total seven lines were identified in the spectrum of the thin film. This is in agreement with the earlier VASP study[83] and the theoretical expectation of the possible orientations for the quadrupolar tensor for the various As sites in $\text{As}[\text{Al}_n\text{Ga}_{4-n}]$ ($n = 0, 1, 2, 3, 4$) in the unit cells [see Fig. 3.2].

Figs. 3.4(b), (c), and (d) display the summed Hahn-Echo spectra for $\text{Al}_{0.522}\text{Ga}_{0.478}\text{As}$ at film orientations $\alpha_{CL} = 30^\circ$, $60^\circ$ and $90^\circ$ respectively. The resonances of different As sites which extensively overlapped in the powder study can now clearly be distinguished. Moreover, because of the single crystalline nature of the spectra it is possible to assign the various predicted quadrupolar tensor orientations for each of the As sites with different coordination. We can now follow the trajectories of all the NMR resonances with varying $\alpha_{CL}$ angle for the rotation of the film. This makes it possible to independently estimate the quadrupolar parameters of the $n = 1$, 2, and 3 sites and compare their relative intensities and line broadenings. As has been discussed extensively in the powder study[83], the quadrupolar interactions of the different $^{75}\text{As}$ coordinations show a distribution in their quadrupolar interaction parameters due to the disorder in the higher coordination spheres as a result of the positioning of Al and Ga over the lattice. In the powder the line broadening due to this structural disorder is convoluted with the powder orientation distribution of the resonances. The thin film experiments make it possible to access the distribution in quadrupolar interaction parameters directly, however.

We can clearly observe strong shifts of the resonance lines for the sites with $n = 1$, 2, and 3 by physically rotating the thin film with respect to the external magnetic field. The quadrupolar parameters for each site were estimated from the experimental NMR resonance positions at different $\alpha_{CL}$ angles (Table. 3.2) which are similar to the values measured in the powder sample. We plot the experimental NMR resonance positions at various $\alpha_{CL}$ angles in Fig. 5a and compared these
with the simulated rotation patterns generated using the quadrupolar parameters obtained from the powder study[83] to judge the correctness of these parameters.

The most striking feature of the $^{75}$As NMR spectra is the large line width of the resonances at all $\alpha_{CL}$ angles. This is most pronounced for the line corresponding to the As[Al$_2$Ga$_2$] coordination site with tensor orientation defined by $\alpha_{PC} = 0^\circ$ and $\beta_{PC} = 45^\circ$ that is significantly broader than all the other resonances. This is an intriguing observation as the first shell configurations of quadrupolar tensors with $\alpha_{PC} = 0^\circ$ and $\beta_{PC} = 45^\circ$ and $\alpha_{PC} = 90^\circ$ and $\beta_{PC} = 45^\circ$ are in principle identical except for their relative orientation. Now, the question is whether these line widths are the results of a random distribution of Al and Ga over the lattice or whether other local interactions are at play.

The simulated line widths of the various resonances using the quadrupolar distribution values as determined from the powder study[83] are substantially narrower, however, than those found experimentally for the thin film. This can hardly be the result of local order as this would lead to line narrowing rather than broadening. The origin of NMR line widths was further investigated by DFT calculations. The structural models used for these calculations are slightly different from those of our previous study[83]. The improved experimental resolution of the thin film studies has prompted a reconsideration of the effect of small structural relaxations that we have neglected in Ref. [83]. The experimental GaAs and AlAs lattice constants are nearly identical, 5.66140 Å and 5.66949 Å respectively[35]. We cannot reproduce such a subtle difference in lattice constants with DFT relaxation. Instead, we used simple harmonic pair-potentials, with an equilibrium distance of $\sqrt{3}/4 \times 5.66140$ Å ($\sqrt{3}/4 \times 5.66949$ Å) for the GaAs (AlAs) bond and followed the computational approach as outlined in section 3.5.2.

Table 3.3 shows the calculated average $^{75}$As C$_Q$ values with and without[83] structural relaxation. The nuclear quadrupole moment from Ref. [93] was used to convert EFG to C$_Q$ values. The average C$_Q$ values slightly decrease upon relaxation, but their variation over the lattice is clearly larger. Apart from this model, we also tried to optimize the atomic positions using DFT (yielding an incorrect ordering of AlAs and GaAs bond lengths) and made a volume-conserving model with uniaxial deformation ($a = b \neq c$). However, neither resulted in a further improvement of the match with the NMR data.

Fig. 3.5(b) shows the theoretical rotation patterns of the NMR resonances generated using EFG parameters ($V_{XX}$, $V_{YY}$, $V_{ZZ}$ and $\alpha_{PC}$, $\beta_{PC}$, $\gamma_{PC}$) obtained from the DFT quantum mechanical calculation as described above. We observe that the theoretical rotation patterns match relatively well with the actual experimental shifts of all the NMR resonances at every orientation. More important, similar to the experimental observation, we notice that the theoretical line width of the NMR resonance for the orientation defined by $\alpha_{PC} = 0^\circ$ and $\beta_{PC} = 45^\circ$ is much larger than all the other NMR resonances. Hence, though the theoretical NMR line width for the $\alpha_{PC} = 0^\circ$ and $\beta_{PC} = 45^\circ$ orientation ($\sim 170$ kHz) is somewhat smaller than the experimental line width ($\sim 250$ kHz), theory does predict that this particular NMR resonance displays $\sim 3$ to 4 times larger line width at $\alpha_{CL} = 0^\circ$ compared to all the other NMR resonances. In fact, the theoretical ratios of the line widths of all the NMR resonances at every $\alpha_{CL}$ orientation match quite well with the actual experimental ratios of the line widths. In Table 3.4 we summarize the experimental and simulated linewidths of the various NMR resonances at $\alpha_{CL} = 0$. It is evident from Table 3.4 that indeed
the experimental and theoretical ratios of linewidths correspond well to each other. This holds true at all \( \alpha_{CL} \) values as can be judged from Figure 3.5. All these observations point to the fact that local distortions of the \( \text{As}[\text{Al}_x\text{Ga}_{1-x}] \) tetrahedra as predicted by the structural relaxations in the model indeed add a major contribution to the line widths of the NMR resonances on top of the contribution due to the positional disorder of Al and Ga in the higher coordination spheres of each As site (Table 3.4).

The simulated rotation patterns with and without distribution in quadrupolar interaction parameters (Figs. 3.5a and b) predict that the resonance lines corresponding to the coordination site \( \text{As}[\text{Al}_1/\beta\text{Ga}_{3/1}] \) with EFG tensor orientations \( \alpha_{PC}=135^\circ, \beta_{PC} = 54.7^\circ \) and \( \alpha_{PC}=225^\circ, \beta_{PC} = 125.3^\circ \) are close to each other for each orientation. Experimentally we do indeed observe that these resonance lines overlap with each other at three of the four \( \alpha_{CL} \) angles, resulting in broad lines. Only at \( \alpha_{CL}=60^\circ \) (Fig. 3.4(c)) we managed to partially resolve these two resonance lines.

All the spectra of the film at different orientations with respect to the magnetic field (\( \alpha_{CL} \) angle) show two narrow resonances separated by \( \delta = 188 \pm 5 \) ppm (at 19.96 T, \( \delta = 27.4 \pm 0.7 \) kHz). These lines are assigned to \( \text{As}[\text{Ga}_4] \) and \( \text{As}[\text{Al}_4] \) sites having a symmetric first coordination shell. Despite their symmetric first coordination spheres, these sites experience quadrupolar interactions, again due to the disorder in the higher coordination spheres. In absence of specific order in the AlGaAs lattice this distribution should be isotropic i.e., rotation invariant which is indeed what we observe in the thin film data; relatively broad lines which remain at the same position for all film orientations \( \alpha_{CL} \). Hence we do not include these two lines in Figs. 3.5(a) and (b). It is furthermore interesting to note that the line widths of the isotropic peaks both in powder and in thin film are of comparable magnitude (of the order of 22 kHz). These observations are a strong indication for the disorder in the lattice to be completely isotropic or in other words the Al and the Ga nuclei are randomly distributed over their lattice sites and there is no preferential stacking.

We finally performed a quantitative analysis of the order-disorder in the lattice by imposing order parameter models analogous to the method used by Tycko et al. [43]. Here we considered two order parameter models, CuPt ordering with diagonal planes stacked in the (111) direction and a CuAu ordering with alternating planes in \( \langle 001 \rangle \). The presence of order in the sample is reflected in the statistics of the occurrence of the various coordinations, \( n \) and the probabilities \( p_n \) for the occupations of the \( \text{As}[\text{Al}_x\text{Ga}_{1-x}] \) sites are equal to the relative intensities of various sites. These probabilities are drawn as solid lines in Fig. 3.6. The shaded areas in this figure represent the NMR line intensities as obtained by directly integrating the spectra (the width of the experimental areas reflect the uncertainties in the procedure). Fig. 3.6 shows that for \( \text{Al}_{0.322}\text{Ga}_{0.478} \)As thin film no satisfactory single value of \( S \) can be obtained using any of the two order parameter models. The obvious reason for this mismatch is the imperfect excitation of various sites in the experiment. We can not directly compare the relative line intensities with the probabilities from the order parameter model. Although we used an RF-field strength that ensures selective excitation of the central transition of the sites with large quadrupolar interactions this is not the case for the symmetric \( \text{As}[\text{Ga}_4] \) and \( \text{As}[\text{Al}_4] \) resonances which have much smaller quadrupolar interactions. Moreover considering the large spectral distribution of the resonances, resonance offsets do affect the line intensities. Therefore, we investigated the effect of experimental conditions such as RF amplitude, resonance offsets, and spectral widths on the relative intensities of the NMR lines of various sites numerically. We simulated

\( \alpha \)
the relative intensities of the various peaks in the Al$_{0.522}$Ga$_{0.478}$As thin film incorporating the exact experimental conditions (RF amplitudes, pulse lengths, offsets and spectral widths) in the SIMPSON simulation package, including the distributions in quadrupolar parameters (distributions in $C_Q$, $\eta_Q$, and Euler angles) as obtained from the DFT calculations into the simulations. The calculations were performed for each site separately and the outcome of these calculations can then be used to determine the relative intensities of the NMR resonances by weighing with the corresponding statistical values ($p_n$) of the occurrence of each site given the order parameter. The simulated and experimental relative intensities are presented in Table. 3.5 and Fig. 3.6 (as diamonds). It is clear from Table. 3.5 and Fig. 3.6 that the simulated results correspond very well with the experimental findings. Finally Fig. 3.7 shows the simulated spectrum for the $S = 0$ condition. So we conclude that the experimental line intensities do not indicate any specific order in the positional distribution of Al and Ga over the lattice as is corroborated by the fact that the resonance lines of the symmetric As[Ga$_4$] and As[Al$_4$] sites do not show variations in position or line width as a function of orientation.

3.7 Conclusions

Observation of $^{75}$As NMR spectra can be a daunting task due to the low NMR receptivity of the $^{75}$As nucleus combined with its large quadrupolar moment often resulting in very large line widths even at high external magnetic field strengths. Nevertheless we show that miniaturization of the detection geometry makes it possible to acquire $^{75}$As NMR spectra of Al$_x$Ga$_{1-x}$As. The high in plane "surface" sensitivity of the stripline probe even allows the study of the limited amount of material available from a single oriented thin film. Since the spectra are relatively well-resolved and not convoluted with the orientational distribution of a powder, it becomes much easier to measure the relative intensities of each NMR line. Further, we can separately identify the predicted EFG tensor orientations for each of the As coordination sites, and clearly follow the trajectories of their NMR resonances as the orientation of the thin film with respect to the external magnetic field is varied. This made it possible to independently and accurately estimate quadrupolar parameters of all the individual NMR resonance lines, including the distribution in quadrupolar interaction parameters which are a result of the positional disorder of Al and Ga over the lattice.

It is intriguing to observe the large line width of all NMR resonances in this oriented material. Particularly the line corresponding to As[Al$_2$Ga$_2$] coordination site with tensor orientation defined by $\alpha_{PC} = 0^\circ$ and $\beta_{PC} = 45^\circ$ is very broad. This is not only due to the disorder in the lattice. It is found that structural relaxations are needed in the DFT quantum mechanical calculations despite of the fact that the Al and Ga atomic radii are nearly identical as are the experimental GaAs and AlAs lattice constants. Apparently the mixed coordinations of As with Al and Ga do cause small but significant distortions of the local tetrahedral symmetry of each As site, thus affecting the width of the distributions in quadrupolar interaction parameters of the differently coordinated As sites. These local structural variations adequately explain the variable line widths of different NMR resonances including that of the As[Al$_2$Ga$_2$] with the orientation $\alpha_{PC} = 0^\circ$ and $\beta_{PC} = 45^\circ$.

Using order parameter models for the order/disorder in the Al$_{0.522}$Ga$_{0.478}$As thin film structure, show that there is no indication of specific local ordering in the position of Al and Ga in the lattice
of the Al$_{0.522}$Ga$_{0.478}$ material. The experimental line intensities of the various As sites observed in the spectra comply with simulated line intensities, incorporating the exact experimental conditions, assuming the absence of positional order i.e. $S = 0$. This is in agreement with the fact that the line widths of the symmetric As[Ga$_4$] and As[Al$_4$] sites are comparable in powder and thin film and do not show any orientational variation.

We feel the present work is a proof of principle of the capabilities of NMR to study III-V semiconductor thin film materials. In its current implementation NMR should be able to contribute to the structural characterization of various relevant inorganic semiconductor materials and answer questions in relation to their functional behavior.

### 3.8 Acknowledgements

We are grateful to G. Janssen and J. van Os for their technical support. We also appreciate the support of Dr. Dennis Grimminck and Prof. Dr. Leo Meerts with fitting the NMR spectra. This work has been supported by EuroMagNET under the EU contract no 228043. Furthermore we acknowledge the support of the Dutch Organization for scientific research (NWO) for support of the “solid-state NMR facility for advanced materials science”. The DFT work is part of the research programme of the “Stichting voor Fundamenteel Onderzoek der Materie (FOM)”, with financial support from NWO.

### 3.9 Appendix

In the Principle Axes Frame, the fourth rank tensor $W$ can be written as,

\[
W_{\eta,0}^{PAS} = \frac{\sqrt{5}}{10} (eq)^2 (\eta^2 + 3)
\]

\[
W_{2,0}^{PAS} = \frac{1}{\sqrt{14}} (eq)^2 (\eta^2 - 3)
\]

\[
W_{2,\pm1}^{PAS} = 0
\]

\[
W_{2,\pm2}^{PAS} = \sqrt{\frac{3}{7}} (eq)^2 \eta
\]

\[
W_{4,0}^{PAS} = \frac{1}{\sqrt{70}} (eq)^2 (1/2\eta^2 + 9)
\]

\[
W_{4,\pm1}^{PAS} = 0
\]

\[
W_{4,\pm2}^{PAS} = \frac{3}{2\sqrt{7}} (eq)^2 \eta
\]

\[
W_{4,\pm3}^{PAS} = 0
\]

\[
W_{4,\pm4}^{PAS} = \frac{1}{4} (eq)^2 \eta^2
\]
Now, we have to transform the $W$ coefficients from PAF to CRY to LAB frame.

$$W_{0,0}^{LAB} = W_{0,0}^{PAS}$$
$$W_{2,0}^{LAB} = \sum_{k=-2}^{2} W_{2,k}^{CRY} D_{k,0}^2 (\alpha_{CL}, \pi/2, 0)$$
$$W_{2,k}^{CRY} = \sum_{j=-2}^{2} W_{2,j}^{PAS} D_{j,k}^2 (\alpha, \beta, \gamma)$$
$$W_{4,0}^{LAB} = \sum_{k=-4}^{4} W_{4,k}^{CRY} D_{k,0}^4 (\alpha_{CL}, \pi/2, 0)$$
$$W_{4,k}^{CRY} = \sum_{j=-4}^{4} W_{4,j}^{PAS} D_{j,k}^4 (\alpha, \beta, \gamma)$$

which results in,

$$W_{2,0}^{LAB} = a_{2,0} + \sum_{n=1}^{2} \left\{ (a_{2,n} \cos n\gamma + b_{2,n} \sin n\gamma) \sin n\alpha_{CL} \right\}$$
$$W_{4,0}^{LAB} = a_{4,0} + \sum_{n=1}^{4} \left\{ (a_{4,n} \cos n\gamma + b_{4,n} \sin n\gamma) \sin n\alpha_{CL} \right\}$$

with,

$$a_{2,0} = -\frac{2}{16\sqrt{14}} (eq)^2 [ (\eta^2 - 3)(1 + 3 \cos 2\beta) + 12\eta \cos 2\alpha \sin^2 \beta ]$$
$$a_{2,1} = 0$$
$$a_{2,2} = -\frac{3}{\sqrt{14}} (eq)^2 \eta \sin 2\alpha \cos \beta$$
$$b_{2,1} = 0$$
$$b_{2,2} = -\frac{3}{4\sqrt{14}} (eq)^2 [ \eta \cos 2\alpha (3 + \cos 2\beta) + (\eta^2 - 3) \sin^2 \beta ]$$
and,

\[ a_{4,0} = \frac{3}{1024\sqrt{70}} (eq)^2 [3(54 + 3\eta^2 + 60\eta \cos 2\alpha + 35\eta^2 \cos 4\alpha) \\
+ 20(18 + \eta^2 + 12\eta \cos 2\alpha - 7\eta^2 \cos 4\alpha) \cos 2\beta \\
+ 70(-3 + \eta \cos 2\alpha)^2 \cos 4\beta] \]

\[ a_{4,1} = 0 \]

\[ a_{4,2} = \frac{1}{16} \sqrt{\frac{5}{14}} (eq)^2 \eta \sin 2\alpha \cos \beta (-9 + 21 \cos 2\beta + 14 \eta \cos 2\alpha \sin^2 \beta) \]

\[ a_{4,3} = 0 \]

\[ a_{4,4} = -\frac{1}{32} \sqrt{\frac{35}{2}} (eq)^2 \eta \sin 2\alpha \cos \beta [\eta \cos 2\alpha (3 + \cos 2\beta) + 6 \sin^2 \beta] \]

\[ b_{4,1} = 0 \]

\[ b_{4,2} = \frac{1}{64} \sqrt{\frac{5}{14}} (eq)^2 [3\eta \cos 2\alpha (5 + 4 \cos 2\beta + 7 \cos 4\beta) + \{ 7\eta^2 \cos 4\alpha (3 + \cos 2\beta) \\
+ (18 + \eta^2)(5 + 7 \cos 2\beta) \}\sin^2 \beta] \]

\[ b_{4,3} = 0 \]

\[ b_{4,4} = -\frac{1}{1024} \sqrt{\frac{35}{2}} (eq)^2 \eta^2 \cos 4\alpha (35 + 28 \cos 2\beta + \cos 4\beta) + 48 \eta \cos 2\alpha (3 + \cos 2\beta) \sin^2 \beta \]

\[ + (18 + \eta^2) \sin^4 \beta] \]

Hence the analytical expression for \( W_{2,0} \) becomes,

\[ W_{2,0}^{LAB} = -\frac{1}{8\sqrt{14}} (eq)^2 [\eta^2 - 3)(1 + 3 \cos 2\beta) + 12 \eta \cos 2\alpha \sin^2 \beta] \]

\[ -\frac{3}{\sqrt{14}} (eq)^2 \eta \sin 2\alpha \cos \beta] [\cos 2\gamma \sin 2\alpha_{CL} + \sin 2\gamma \cos 2\alpha_{CL}] \]

\[ -\frac{3}{4\sqrt{14}} (eq)^2 [\eta \cos 2\alpha (3 + \cos 2\beta) + (\eta^2 - 3) \sin^2 \beta] [\sin 2\gamma \sin 2\alpha_{CL} - \cos 2\gamma \cos 2\alpha_{CL}] \]
and that for \( W_{4,0} \),

\[
W_{4,0}^{LAB} = \frac{3}{1024\sqrt{70}} (eq)^2 \left[ 3(54 + 3\eta^2 + 60\eta \cos 2\alpha + 35\eta^2 \cos 4\alpha) + 20(18 + \eta^2 + 12\eta \cos 2\alpha

- 7\eta^2 \cos 4\alpha) \cos 2\beta + 70(-3 + \eta \cos 2\alpha)^2 \cos 4\beta \right] +

\frac{1}{16} \sqrt{\frac{5}{14}} (eq)^2 \left[ \eta \sin 2\alpha \cos \beta(-9 + 21 \cos 2\beta + 14\eta \cos 2\alpha \sin^2 \beta)(\cos 2\gamma \sin 2\alpha_{CL} +

\sin 2\gamma \cos 2\alpha_{CL}) + \frac{1}{4}(3\eta \cos 2\alpha(5 + 4 \cos 2\beta + 7 \cos 4\beta) + (7\eta^2 \cos 4\alpha(3 + \cos 2\beta)

+(18 + \eta^2)(5 + 7 \cos 2\beta) \sin^2 \beta)(\sin 2\gamma \sin 2\alpha_{CL} - \cos 2\gamma \cos 2\alpha_{CL}) \right] +

\frac{1}{32} \sqrt{\frac{35}{2}} (eq)^2 \left[ \frac{1}{32}(\eta^2 \cos 4\alpha(35 + 28 \cos 2\beta + \cos 4\beta) + 48\eta \cos 2\alpha(3 + \cos 2\beta) \sin^2 \beta +

+(18 + \eta^2) \sin^4 \beta)(\cos 4\gamma \sin 4\alpha_{CL} + \sin 4\gamma \cos 4\alpha_{CL}) + \eta \sin 2\alpha \cos \beta \{\eta \cos 2\alpha(3 +

\cos 2\beta) + 6 \sin^2 \beta\}(\sin 4\gamma \sin 4\alpha_{CL} - \cos 4\gamma \cos 4\alpha_{CL}) \right]
\]
3.9. APPENDIX

Figure 3.7: (a) Experimental $^{75}$As Hahn-echo spectrum (19.96 T, 82000 scans at $\alpha_{CL} = 0^\circ$) of Al$_{0.522}$Ga$_{0.478}$As, (b) Numerically simulated $^{75}$As spectra of Al$_{0.522}$Ga$_{0.478}$As. The simulation was done assuming an order parameter $S = 0$. The line widths are generated from the distributions in EFG parameters obtained from the DFT calculations, (c) Individual constituent NMR lines of the summed spectrum in (b) showing the different $^{75}$As[$Al_nGa_{4-n}$] coordination sites.
Chapter 4

A Multi-Nuclear Magnetic Resonance Investigation of the Atomic Ordering of In_{0.483}Ga_{0.517}P Grown by Vapor Phase Epitaxy

4.1 Abstract

In this paper the short and long range order in In_{0.483}Ga_{0.517}P thin films is investigated by solid-state Nuclear Magnetic Resonance (NMR). To this end two samples were grown on a GaAs substrate with Metal-Organic Vapor Phase Epitaxy at two different growth pressures. From band gap energy measurements, CuPt Long Range Order parameters of $S_{CuPt} = 0.22$ respectively 0.39 were deduced. In the $^{31}$P spectrum five resonances are observed corresponding to the five possible P(Ga$_n$In$_{4-n}$), $n = 0...4$ coordinations whose relative intensities correspond to the order in the material, but the intensity variations for order parameters between 0 and 0.5 are minimal. $^{69}$Ga, $^{71}$Ga and $^{115}$In (MQ)MAS spectra were acquired to analyze the quadrupolar and chemical shift distributions related to the (dis)order in these materials in more detail. All these spectra clearly reflect the disorder in the sample and don’t show the presence of highly ordered domains. The difference in order parameter in the sample is not clearly reflected in the spectra. The Electronic Field Gradients (EFGs) of Indium and Gallium were calculated using Density Functional Theory, showing that the $^{69}$Ga, $^{71}$Ga and $^{115}$In quadrupolar parameters are dominated by variations in the first coordination sphere. The effect of disorder indirectly influences the Electric Field Gradients at the sites of the nuclei by causing variations in their first coordination sphere. The large sensitivity of the EFGs toward minute changes in the coordination make it difficult to obtain quantitative agreement between theory and

experiment. Finally $^{31}$P chemical shift calculations nicely reproduced the experimentally observed trend. Upon structural relaxation the experimentally observed shift are well reproduced confirming the assignment of the resonances. The $^{31}$P chemical shifts are very sensitive to changes in the lattice parameter. The difference in lattice parameter of InP and GaP explains their small experimental difference in chemical shift where a large difference would be expected based on the observed shift difference of the P[In$_4$] and P[Ga$_4$] coordinations in InGaP.

4.2 Introduction

As has been reviewed by Yesinowski[94, 95] there is an interest in nanoscaled semiconductors, and with improvements in sensitivity and resolution, the area of semiconductor NMR is being rejuvenated. Spontaneous atomic ordering of semiconductor alloys is of great practical and fundamental interest and the ordering of III-V alloys has been extensively studied. An exemplary III-V semiconductor in which the (spontaneous) formation of CuPt long-range order has been observed[96, 97, 98, 99, 29, 100] is InGaP. InGaP has a strong lattice mismatch of $\sim 7\%$, which leads to stress within in the lattice. Consequently, the atoms will arrange themselves into their most energy favorable positions during growth. Strain-minimizing 3D arrangement can lead to spontaneous ordering[28, 101]

Although a good percentage of the mentioned studies concerned the InGaP long range ordering, complementary, it is necessary to investigate the short range ordering, which in fact can be completely different. For such information, NMR is the ideal candidate, since it probes short range interactions. There have been two relevant NMR investigations of In$_x$Ga$_{1-x}$P. Tycko et al.[43] used $^{31}$P Magic Angle Spinning(MAS) NMR to study atomic ordering in bulk and thin film InGaP. Using the $^{31}$P relative intensities, they determined an upper limit for the long range order parameter $S_{CuPt} < 0.6$. A quantitative assignment of the CuPt long range order parameter based on the relative intensities was not accurate since the dependency of the relative intensities on the order parameter is rather weak for low order parameters. Furthermore, their assignment of the relative intensities was not that accurate since, at that time, the spinning speed was insufficient to avoid overlapping spinning sidebands in the $^{31}$P spectrum.

Mao et al.[100] used the quadrupolar information of $^{71}$Ga, i.e. satellite and central transition ratio under a NMR spin echo, for different rotations and related this to the average LRO. The quadrupolar interaction is sensitive to the local surrounding. Therefore, this interpretation assumes that the short and long range ordering are identical. Their experimentally obtained quadrupolar interaction was compared to a theoretical calculation based on point charges. In 1997, Wei and Zunger showed that in fact their point charge model was insufficient to predict the EFGs correctly and the use of Density Functional Theory(DFT) is required[102] In our earlier work we investigated that the local sensitivity of the quadrupolar interaction in Al$_x$Ga$_{1-x}$As can extend up to the 7$^{th}$ shell[83] and is a good probe of the local order in the material, particularly when intact oriented thin films are studied.[103]

In this work we acquired $^{31}$P, $^{69/71}$Ga and $^{115}$In NMR data to analyze the short and long range order in In$_{0.483}$Ga$_{0.517}$P. As mentioned before, NMR offers good possibilities to study III-V semi-
Table 4.1: Comparison of the MOVPE growth parameters of InGaP and resulting band gap in this study and the work by Tycko et al.\cite{tycko} An important feature is the substantial difference in growth rate. Sample W20 was grown with relatively low ordering at a pressure of 20 mbar and sample W50 with a higher ordering at 50 mbar pressure

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</tr>
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<tbody>
<tr>
<td>film size</td>
<td>7-15 $\mu$m $2\times2$ cm$^2$</td>
<td>5 $\mu$m $2''$ wafer</td>
</tr>
<tr>
<td>composition</td>
<td>In$<em>{0.485}$Ga$</em>{0.515}$P</td>
<td>In$<em>{0.483}$Ga$</em>{0.517}$P</td>
</tr>
<tr>
<td>carrier conc.</td>
<td>1...5 \times 10^{16} cm$^{-3}$</td>
<td>10$^{14}$...10$^{15}$ cm$^{-3}$ n-type</td>
</tr>
<tr>
<td>growth [$\mu$m/h]</td>
<td>6</td>
<td>1.6</td>
</tr>
<tr>
<td>temp. [°C]</td>
<td>600, 670, 625, 690</td>
<td>650</td>
</tr>
<tr>
<td>band gap [eV]</td>
<td>1.88, 1.81-1.82</td>
<td>1.886 (W20), 1.809 (W50)</td>
</tr>
</tbody>
</table>

Conductors, since in contrast to X-ray, Photoluminescence (PL) and Photoluminescence Excitation (PLE) and other studies, NMR is sensitive to short-range interactions. These short-range interactions are manifested in a spectrum via the chemical shift, exchange, dipolar and/or quadrupolar interactions. Furthermore, the occurrences of sites in a spectrum are related to contributions over the volume of the sample. If these occurrences do not deviate from the long range scale, the same ratios can be used as a measure for the long range order (LRO).\cite{tycko, caruso, lang} To resolve the spectra of Gallium and Indium we resorted to MQMAS, this technique can separate the chemical shift information from the quadrupolar distribution. Different charge distributions throughout the lattice give rise to different Electronic Field Gradient distributions in case of a (generally speaking) inhomogeneous, partially ordered InGaP lattice. The quadrupolar interaction probes the local configuration. In randomly ordered alloys quadrupolar distributions are therefore expected. Density Functional Theory (DFT) can be used to simulate EFG values and distributions. In the present study we employ VASP,\cite{vasp1, vasp2, vasp3, vasp4, vasp5} as it allows EFG and chemical shift calculations of a periodic lattice with any type of ordering. The distribution in the interaction parameters can then be interpreted in relation to the disorder in the lattice.\cite{vasp6, vasp7, vasp8, vasp9}

4.3 Experimental & methods section

Two samples were grown using undoped $2''$, 350 $\mu$m thick, GaAs wafers with crystal orientation (100), $2^{\circ}$ off towards (110) as substrates. The two samples consisted of a 0.5 $\mu$m GaAs buffer layer, a 10 nm AlAs layer and a 5 $\mu$m undoped InGaP top layer. The substrate and buffer layer were etched from the backside with a citric acid - hydrogen peroxide solution (5:1) for several days, leaving a freestanding InGaP thin film. The first sample, denoted as W20, was grown with relatively low ordering at a pressure of 20 mbar and the second sample, W50, with a higher ordering at 50 mbar, see Table 4.1. An indication for the long range ordering was obtained by measuring the electronic band gap at 300 K. Using $\Delta E_g = -484.55^2 + 4.354 S^4 - 174.45 S^6$, see ref.\cite{vasp10}, an average LRO parameter of 0.22 respectively 0.39 was determined. The InGaP thin films ($\sim$mg quantities containing of the order of $10^{17}$ spins) were crushed into powder samples with a typical grain size of a few micrometers and subsequently transferred to PEEK sample holders for NMR measurements.

InGaP crystal lattice is represented in Figure 4.1. In fully CuPt ordered In$_{x}$Ga$_{1-x}$P, alternating
layers of Ga and In atoms can be expected along the (111) direction. The lattice spacing for InP is 5.8687 Å and for GaP 5.4505 Å. The lattice spacing can be matched to the GaAs substrate lattice spacing of 5.6533 Å for \( x = 0.483 \).

### 4.3.1 NMR experiments

The two powder samples were placed in 2.5 mm (outer diameter, inner diameter 1.5 mm) rotors in a T3 dual channel HX MAS probe. The sample length in the rotor was 1 mm, the volume 1.8 mm\(^3\). The \( T_1 \) values of the individual \(^{31}\)P sites of the W20 sample were estimated to range from 430 to 500 seconds, with an accuracy of \( \pm 80 \) seconds. The average, integrated \( T_1 \) was determined to be 470\( \pm \)70 seconds using saturation recovery. Both samples were spinning at 25 kHz to avoid spinning sideband overlap in the \(^{31}\)P spectra acquired at 9.4 Tesla. The \(^{31}\)P chemical shifts are referenced with respect to H\(_3\)PO\(_4\) (0 ppm) [43, 106]. Because of the very long \(^{31}\)P spin-lattice relaxation times, quantitative \(^{31}\)P spectra were obtained using 80 acquisitions with 10\(^6\) pulses and a pulse delay of 1000 seconds. An exponential broadening of 500 Hz was applied prior to Fourier transformation. In the \(^{31}\)P spectra, the width, the relative intensity, the ratio Gaussian / Lorentzian and the chemical shift were least square fitted for each of the five sites.

The spin-lattice relaxation times of \(^{69}\)Ga and \(^{71}\)Ga were determined to be less than 0.5 seconds. We determined the \(^{71}\)Ga GaAs shift to be 215\( \pm \)1 ppm, in agreement with Han \textit{et al.}[68] and Potter \textit{et al.}[107] who reported 216 ppm for the \(^{71}\)Gallium chemical shift of GaAs. To analyse the Gallium line broadening mechanisms i.e. to separate the Gallium quadrupolar distribution from the chemical shift distribution, we first recorded \(^{71}\)Ga 3QMAS z-filtered spectra of both samples. The 3QMAS pulse sequence was \( p_c \cdot t_1 \cdot p_c \cdot \tau \cdot p_{90} \cdot \text{acq} \), in which \( p_c \) the triple quantum excitation pulse time, \( p_c \) the conversion pulse time and \( p_{90} \) the 90 degree pulse for z-filtering. States acquisition was used and a 24 step phase-cycling in 60° steps to refocus the triple quantum coherences to the -1 quantum coherence. Because of the difference in quadrupolar moment, \(^{69}\)Ga 1D MAS spectra were obtained at 9.4 \( T \) and 14.1 \( T \) for comparison with the \(^{71}\)Ga MQMAS result. A static spectrum was recorded to obtain additional information on the extent of dipolar and exchange interactions. Finally a \(^{69}\)Ga nutation spectrum was obtained to verify the quadrupolar interaction and its distribution.
Table 4.2: Calculated $V_{zz}$ in $10^{20}$ V/m$^2$ for perfect CuPt-like ordering using the LDA. FLAPW results of Wei & Zunger[102] and our PAW results using the same structure (i.e. with ideal $c/a = \sqrt{8/3}$, $a = 4.0100 \times 10^{10}$ m).

<table>
<thead>
<tr>
<th></th>
<th>FLAPW (ref. [102])</th>
<th>PAW</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>6.7</td>
<td>6.7</td>
</tr>
<tr>
<td>Ga</td>
<td>-11.7</td>
<td>-11.7</td>
</tr>
<tr>
<td>P[Ga$_3$In]</td>
<td>-12.1</td>
<td>-11.5</td>
</tr>
<tr>
<td>P[GaIn$_3$]</td>
<td>13.3</td>
<td>12.6</td>
</tr>
</tbody>
</table>

The $T_1$ of $^{115}$In ($I = 9/2$) of the W50 sample was determined to be 0.11 seconds using saturation recovery. $^{115}$In 3QMAS spectra were recorded, using the z-filtered 3QMAS pulse sequence.

4.3.2 DFT calculations

Calculations were carried out with the Vienna *ab initio* simulation programme (VASP)[52, 53, 54, 55] using the Projector-Augmented Wave (PAW) method.[61, 62] The EFG tensors were calculated with the method of Ref. [51]. For chemical shift calculations gauge-including PAW (GIPAW) linear response was employed.[108, 109]

The PAW data sets had frozen [Ar], [Kr] and [Ne] cores for Ga, In and P respectively. All data sets had two augmentation channels per each angular momentum $\ell$. For Ga and In augmentation partial waves for $\ell = 0, 1, 2$ were included and the $f$-channel acted as local pseudopotential. For phosphorous only $\ell = 0, 1$ partial waves were used and the $d$-channel was the local pseudopotential. We tested unfreezing the semi-core Ga-3p and In-4p states. These states affect the EFGs up to $\sim 10\%$. These core states were kept frozen in all other calculations.

The Becke-Perdew-Ernzerhof (PBE)[110] exchange-correlation functional was used (except for some test calculations), In the supercells employed for the random models (32 f.u.) the k-point mesh varied between $2 \times 2 \times 2$ (EFGs only) and $4 \times 4 \times 4$ (EFGs and structural relaxation). The plane wave energy cutoff was 280 eV. For the GIPAW calculations a higher cutoff of 400 eV was needed and a $4 \times 4 \times 4$ Monkhorst Pack[111] k-point mesh was found to be sufficient for the random models.

In Table 4.2 we compare our EFG PAW results with the Full-potential Linearized Augmented Plane Wave (FLAPW) results of Wei & Zunger [102] who considered InGaP$_2$ with perfect CuPt order. Both calculations neglect the effect of semi-core states. Indeed, for both In and Ga the PAW and FLAPW EFGs are practically identical. For phosphorous PAW and FLAPW yield slightly different results, which is probably due to the lack of a phosphorous $d$-channel in our PAW data set.

Our (PBE) optimized lattice constants are $5.51 \times 10^{-10}$ m and $5.96 \times 10^{-10}$ m for GaP and InP respectively. This is in very good agreement with accurate FLAPW+lo calculations that give $5.514 \times 10^{-10}$ m and $5.968 \times 10^{-10}$ m.[112] The experimental lattice constants are $5.4505 \times 10^{-10}$ m and $5.8687 \times 10^{-10}$ m (at 300 K).[113] In this study we work with experimental lattice constants whenever possible.
Table 4.3: Fitted parameters of the sites P[GaₙIn₄₋ₙ] obtained with least square fitting, $x = 0.483$. The relative intensities were fixed, corresponding with $S_{CuPt}=0.22$ (up) sample W20 and $S_{CuPt}=0.3$ (down) sample W50. Ratio(L/G) is the ratio of a Lorentz / Gaussian function.

<table>
<thead>
<tr>
<th>n</th>
<th>rel. int.</th>
<th>c.s. (ppm)</th>
<th>width (kHz)</th>
<th>ratio(L/G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
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<td>2.3±0.5</td>
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<tr>
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<tr>
<td>0</td>
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<td>4.2±0.5</td>
<td>0.93</td>
</tr>
</tbody>
</table>

4.4 NMR Results

4.4.1 $^{31}$P NMR

Figure 4.2 displays the $^{31}$P single pulse excitation (SPE) MAS NMR spectra of samples W20 and W50, whereas the result of their deconvolution are presented in table 4.3. The spectra were fitted by fixing the relative intensities of the five sites according to the CuPt long range order parameter [43, 42] as obtained from the band gap measurements, while leaving line width and position as free fit parameters. With these relative intensities, the $^{31}$P spectra fitted reasonably well. In accordance with the observation by Tycko et al. [43] we observe that the full width at half maximum (FWHM) of the P[GaₙIn₄₋ₙ] site increases with an increasing number of Indium ($I = 9/2$) atoms in the first coordination sphere. This might indicate that the line width is still influenced by residual dipolar couplings and/or exchange interactions with the In atoms, despite the fact that the spinning speed in the present study is substantially higher than in the study by Tycko et al. The static dipolar coupling can be estimated from second moment theory. Because $^{115}$In has $I = 9/2$ and $\gamma = 5.8972 \times 10^7 \text{rad/(Ts)}$, the dipolar coupling for P[In₄], calculated in an fcc lattice up to the 6th sphere is 7.1 kHz, while second moment theory indeed predicts a much lower dipolar coupling of 3.4 kHz for P[Ga₄] [114]. Although the spinning speed (25 kHz) is substantially higher than these dipolar couplings they may still not be fully averaged as the observed trend in line width follows the calculated dipolar couplings. In any case, the width of the $^{31}$P resonances is dominated by a distribution in chemical shift due to varying higher-order coordinations of the sites related to the positional disorder of In and Ga over the lattice. This is corroborated by the fact that the width of the narrowest resonance, assigned to P[Ga₄], is best described by a Gaussian line shape. Therefore the variations in line width for the different phosphorus coordinations in the spectra might also be due to a difference in their sensitivity towards variations in their higher coordination spheres e.g. leading to variations in bond angles and bond distances in the first coordination sphere (vide infra).

The chemical shift values of the different $^{31}$P resonances of sample W50 are on average 1.6 ppm
Figure 4.2: $^{31}$P experimental spectra of the samples W20 (top) and W50 (bottom). The fitted resonances of the five sites are dotted. The label $n$ indicates the site $P[Ga_nIn_{4-n}]$. The parameters obtained from these fits are displayed in Table 4.3. The relative intensities of the sites were fixed according to the CuPt order parameters of $S = 0.22$ and $S = 0.39$ for W20 and W50 respectively. This yielded satisfactory fits as is clear from the residuals in the figure.

lower than those of sample W20. Tycko et al. related the values of the chemical shift to the overall composition of the sample. They observed that the chemical shift of the $^{31}$P resonances of the different coordinations in the spectra of bulk In$_x$Ga$_{1-x}$P with a composition $x = 0.86$ and films with a composition $x = 0.5$ all differ by about 30 ppm. Assuming a linear relation between the chemical shift and the composition, the spectrum would shift approximately 1.0 ppm per 0.01 increment of $x$. Consequently, the 1.6 ppm average chemical shift difference of samples W20 and W50 could indicate a 0.02 change in composition. Such variation of the composition is possible within the composition-accuracy of the growth process. Assuming a linear relationship between chemical shift and composition is far too simple, as can be seen the shift difference between identical sites in the two samples is different for each specific coordination. Note further that the difference in $^{31}$P chemical shift values of bulk InP (-148 ppm) and GaP (-142 ppm) does not coincide with the difference in chemical shift for the $n = 0$ and $n = 4$ coordinations in the InGaP spectra. The sensitivity of the $^{31}$P shifts implies that $^{31}$P NMR could be exploited as a very sensitive tool for probing the composition of the material once an in-depth theoretical and experimental understanding of the variation of the $^{31}$P shifts with composition has been established. There is only a weak change in the theoretical
relative intensities going from a completely random structure to a CuPt ordered structure with $S$ ranging from 0...0.5,[13, 42] see Fig. 4.3, so $^{31}$P NMR can only give an upper bound for the order parameter. Indeed the spectra of sample W20 and W50 confirm their relatively low average CuPt LRO. It is furthermore not possible to determine the difference in order parameter for these two samples based on relative line intensities, as the relative $^{31}$P intensities in the spectra hardly differ. It should be noted, however, that the line widths and positions of the various $^{31}$P resonance differ subtly between the two samples. This might be related to their difference in overall structure.

### 4.4.2 $^{71}$Ga NMR

$^{71}$Ga SPE MAS and MQMAS NMR spectra were obtained at 14.1T. The MAS spectrum shows a single featureless line. Fig. 4.4 shows the $^{71}$Ga 3QMAS spectrum of sample w50 obtained at 14.1T. The $^{71}$Ga MQMAS spectrum of W20 (not shown) looks very similar. To better visualize the distributions in the NMR parameters the displayed spectral region is focused on the central transition signal only. It can be deduced from these spectra that the $^{71}$Ga line width at 14.1T is dominated by a distribution in chemical shift. Nevertheless, there is also a contribution from (a distribution in) the quadrupolar interaction. The observation of a $^{71}$Ga resonance with a broad distribution in chemical shift and quadrupolar interaction rules out the possibility that the observed order in the material comes from macroscopic domains that are fully ordered. Such domains would display a single chemical shift value and a well-defined quadrupolar interaction with an asymmetry parameter $\eta = 0$. By simulating the MQMAS spectra, including the excitation efficiency at the employed rf-field strength and assuming a simple Gaussian chemical shift distribution, the average $^{71}$Ga isotropic chemical shift, the width of the chemical shift distribution and the average quadrupolar coupling constant could be estimated. The values are displayed in the left column of Table 4.4. It should be noted, however, that it was not possible to obtain a satisfactory fit of the spectra by assuming uncorrelated distributions in chemical shift and quadrupolar interaction. The MQMAS line shape suggests that for higher chemical shift values, smaller quadrupolar interactions are encountered. As
4.4. NMR RESULTS

Figure 4.4: Sheared z-filtered $^{71}$Ga 3QMAS spectrum of sample W50 obtained at 14.1T employing 15 kHz spinning. 20 contour levels are shown from 20 to 100%. The $t_2$ domain signals were apodized by a 500 Hz wide shifting Gauss-function, whereas in the $t_1$ domain a 500 Hz exponential line broadening was applied. 1440 acquisitions, with a relaxation delay of 0.5 second, were accumulated to obtain the spectrum. The first two hard pulses were set to 2.2 $\mu$s and 0.8 $\mu$s respectively with a $\nu_{T_1}$=300 kHz. The selective $z$-filter pulse was set to 8.6 $\mu$s with $\nu_{T_1}$= 15.4 kHz. The $z$-filter echo time was 66 $\mu$s. The total recording time was 16.3 hours.

The resonance does not display any fine structure, it is not possible to evaluate this quantitatively, however.

4.4.3 $^{69}$Ga NMR

Figure 4.5a displays the $^{69}$Ga SPE MAS spectra of samples W20 and W50 recorded at 9.4T. The shape of the resonance shows that the spectra are dominated by the second-order quadrupolar interaction. The typical slope of the right hand flank indicates that there is a substantial distribution in the quadrupolar interaction of the various Ga sites in the sample. The more prominent presence of the quadrupolar broadening in these spectra as compared to the $^{71}$Ga spectra described in the previous paragraph can be explained by the fact that the quadrupolar moment of $^{69}$Ga is 70% larger than that of $^{71}$Ga, and the lower external magnetic field strength (9.4 T vs. 14.1 T) at which these $^{69}$Ga MAS spectra were recorded. An important factor when studying half-integer quadrupolar nuclei using MAS NMR is the spinning speed. For a system with a quadrupolar distribution the spinning speed must be high enough to effectively average the largest quadrupolar interactions encountered in the distribution, otherwise lineshape changes and unresolved sidebands can be encountered, hampering an unambiguous analysis of the lineshape. As can be seen in Fig. 4.5b, for the $^{69}$Ga MAS spectra of W50 recorded at 14.1 T, a spinning speed of 20 kHz was necessary to reach this point. The line width of the $^{69}$Ga MAS spectrum recorded at 14.1 T is slightly narrower than that recorded at 9.4 T (6.1 kHz vs. 6.8 kHz), showing that there is also a sizeable chemical shift distribution as expected. The effect of quadrupolar and chemical shift distributions on the spectra, decrease respectively increase going to higher $B_0$ field. The $^{69}$Ga quadrupolar broadening at 14.1 T is 1.5 times narrower than the broadening at 9.4 T, while the chemical shift distribution increases
Figure 4.5: (top) $^{69}$Ga MAS spectra of W20 and W50 obtained at 9.4 Tesla. The spectra were recorded employing an RF field strength of 67 kHz. The pulse length was 1.85 $\mu$s, the spinning speed 23 kHz, and the pulse delay 1 second. The W20 spectrum was acquired accumulating 43,200 scans and the W50 adding 128 scans. An exponential broadening of 1 kHz was used. The results from the fitted spectrum of the W20 sample are displayed in Table 4.4. The additional narrow line in the spectrum of w50 is due to a GaAs impurity originating from substrate. (bottom) $^{69}$Ga MAS spectra of W50 obtained at 14.1 T at different spinning speeds. 256 acquisitions were acquired with a selective pulse of 2 $\mu$s ($\sim$60°, $\nu_{SF} \approx 40$ kHz). The relaxation delay was 1 second. Exponential line broadening of 500 Hz was applied. A spinning speed well in excess of 15 kHz is needed to avoid line shape variations due to the inefficient modulation of the second-order quadrupolar interaction

1.5 times. The FWHM of the resonances obtained at 9.4 T and 14.1 T are indeed approximately equal to the sum of the quadrupolar and chemical shift broadening expected on the basis of the analysis of the $^{71}$Ga MQMAS spectrum. A fit of the $^{69}$Ga MAS spectra (Fig. 4.5a) nicely reproduced these parameters as is summarized in Table 4.4. No evidence of broadening due to dipolar or exchange interactions is present and thus it is assumed that they play only a minor role.

As further evidence for the dominating quadrupolar broadening of the $^{69}$Ga spectra a nutation spectrum was acquired for sample W50. This sample contained a small GaAs impurity of the substrate wafer. GaAs has a cubic lattice structure and as a result the corresponding Gallium resonance has a near zero quadrupolar interaction. Indeed this resonance (labeled A) nutates at $\nu_A \approx \nu_{SF}$. The Ga resonance of the W50 InGaP material (labeled B) nutates with a frequency $\nu_B \approx \nu_{SF}$.
Figure 4.6: $^{69}$Ga nutation spectrum at 9.4 T of the W50 sample at an rf field strength of $\nu_{rf} = 67$ kHz. Exponential line broadening of 1000 respectively 500 Hz was applied in the $\nu_1$ and $\nu_2$ dimension. There were 20 $d\nu_2 = 2\mu$s increments. Nine contour levels are shown from 20% to 100%. The right side view along $\nu_1$ displays the nutation profile for site B, taken at the position of the dotted line.

$2\nu_{rf}$, showing that the quadrupolar interaction dominates over the rf-field strength $\nu_{rf} \approx 67$ kHz and we are nearly in the selective pulse regime. At this rf-field strength this means that the quadrupolar coupling constant $C_Q$ must be well over 1.5 MHz. The smooth tail to lower frequencies in the nutation profile is due to $\nu$-inhomogeneity and the presence of a distribution in the quadrupolar interaction. The absence of well-defined sharp features is additional evidence for the absence of domains with high order.

The Ga spectra of the samples W20 and W50 clearly show that their lattices are mainly disordered, without the presence of fully ordered domains. The experimental spectra for both samples hardly differ, at best the W20 spectra show a slightly wider tail due to the quadrupolar distribution, but the differences are too insignificant to quantify. So the differences in order parameter of both samples is not clearly reflected in their Ga spectra.

4.4.4 $^{115}$In NMR

The last NMR active isotope in the InGaP system is $^{115}$In. $^{115}$In SPE MAS spectra of W20 and W50 are displayed in Figure 4.7. Both spectra are identical with a slightly asymmetric flank to the high-field side. As $^{115}$In is a quadrupolar ($I = 9/2$) nucleus with a sizeable quadrupolar moment this indicates that the second-order quadrupolar broadening contributes to the line width and that there is a distribution in quadrupolar coupling constant again reflecting the disorder that is present in the samples. This is corroborated by the numerous spinning sidebands that are visible in the spectra which are attributed to the satellite transitions. Additional broadening of the lines might come from a distribution in chemical shift and/or dipolar or exchange interactions. This can be elucidated by MQMAS NMR.

The $^{115}$In 3QMAS spectra of sample W50 is displayed in Figure 4.8. As expected from the analysis of the MAS NMR spectra, a pronounced distribution in the quadrupolar interaction is observed, additionally there is a sizeable distribution in the isotropic chemical shift. The $\nu_1$ and
\( \nu_2 \) sum projections of the MQMAS spectrum of W20 (dotted lines) are shown as well. There are no clear differences between the MQMAS spectra of both samples. No clear contributions from other interactions are visible in the spectra. The chemical shift and quadrupolar parameters were estimated from a simulations as is summarized in Table 4.4. As was the case with the Ga MQMAS NMR spectra, it again proved difficult to get satisfactory fits of the spectra by adding the chemical shift distribution as a Gaussian broadening to the distribution in quadrupolar interaction parameters. This might indicate that there is a correlation between the isotropic chemical shift of Indium at a specific site and its quadrupolar interaction. A simulation of the central transition of the MAS spectrum using the NMR interaction parameters obtained from the MQMAS spectra nicely reproduces the experimentally observed line shape and width (Fig. 4.7).

Comparable to the results that were obtained from the Ga spectra, the \(^{115}\)In spectra of the samples W20 and W50 clearly show the presence of disorder in the samples which is reflected by a distribution in chemical shift and quadrupolar interactions. From the absence of distinct sharp features in the spectra we again conclude that there are no fully ordered domains present in the sample. Unfortunately the spectra of both samples again look identical, meaning that their difference in order parameter is not apparent from their \(^{115}\)In spectra.

Table 4.4: Summary of the experimentally derived NMR values with their estimated accuracies. Note that we measured the absolute, average value of the EFGs. GB means Gaussian Broadening which is half the FWHM or 1.17 times the standard deviation of the distribution.

<table>
<thead>
<tr>
<th></th>
<th>(^{71})Ga 3QMAS</th>
<th>(^{69})Ga MAS</th>
<th>(^{115})In 3QMAS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>600</td>
<td>400/600</td>
<td>600</td>
</tr>
<tr>
<td>(\langle C_q \rangle) (MHz)</td>
<td>1.5 ± 0.2</td>
<td>2.6 ± 0.2</td>
<td>16 ± 1 GB 6 ± 2</td>
</tr>
<tr>
<td>EFG ((10^{20} \times V/m^2))</td>
<td>6.3 ± 0.5</td>
<td>6.3 ± 0.5</td>
<td>8.2 ± 0.6 GB 3 ± 0.8</td>
</tr>
<tr>
<td>(\delta_{iso}) (ppm)</td>
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<td>330 ± 10</td>
<td>744 ± 10</td>
</tr>
<tr>
<td>(\Delta \delta) (ppm)</td>
<td>25 ± 5</td>
<td>25 ± 5</td>
<td>50 ± 5</td>
</tr>
</tbody>
</table>
4.5. DFT MODELING

4.5.1 In and Ga EFGs & chemical shifts

Table 4.5 summarizes the results of the DFT calculations of the Electric Field Gradients at the Gallium and Indium sites in the lattices. First we considered InGaP$_2$ with perfect CuPt-like order. Optimization of the structure resulted in a substantial change of bond lengths and bond angles and dramatically affected the EFGs. For a realistic modelling inclusion of relaxation evidently is crucial. It appears that $V^\text{Ga}_{zz}$ is only appreciably affected by bond angle changes whereas $V^\text{In}_{zz}$ is also affected by bond length changes.

To study the effect of disorder we constructed a model consisting of $2 \times 2 \times 2$ conventional zincblende unit cells. This supercell was periodically repeated. The anion sub-lattice was occupied by phosphorous ions. To model the disorder the In and Ga were placed randomly on the cation sub-lattice, while keeping the constraint on composition, i.e. the supercell has composition In$_{16}$Ga$_{16}$P$_{32}$. We did not allow for distortions of the cubic shape of the super-cell, as in the limit of high disorder only short-range, local anisotropy can survive. Again relaxation had a large effect (compare columns “fixed” and “relaxed” in the right part of Table 4.5). Optimizing the cell volume had a minor effect (not shown).

Going from $S_{CuPt} = 1$ to the disordered model, the average absolute Gallium $V_{zz}$ decreases from 14.0 to $9.7 \times 10^{20}$ V/m$^2$, while the Indium EFG increases from 8.9 to $15.2 \times 10^{20}$ V/m$^2$. 

![Figure 4.8: (top) W20 sheared $^{115}$In $z$-filtered 3QMAS spectrum at 25 kHz spinning. 20 contour levels are shown from 10 to 100%. The $t_2$ domain signals were broadened by a shifting Gauss of 500 Hz, the $t_1$ domain is apodized by 500 Hz exponential broadening. The signal is obtained from 840 acquisitions with a pulse delay of 0.64 second. Dwell times were $dw_1 = 1.6\mu$s and $dw_2 = 4\mu$s, the $t_1$ dimension had 256 increments, using States acquisition. The first two hard pulses were set to 1.04 respectively 0.38 $\mu$s with $\nu_{rf} \approx 300$ kHz. The selective $z$-filter pulse was set to 6 $\mu$s with $\nu_{rf} = 10$ kHz. Z-filter echo time was 40 $\mu$s. The shearing factor was 91/36. The spectral width of $\nu_1$ was scaled by 36/17. The total recording time was 38.8 hours. (bottom) W50 sheared $^{115}$In $z$-filtered 3QMAS spectrum at 25 kHz spinning. Spinning sidebands were visible in the $\nu_1$ dimension. The signal is obtained from 96 acquisitions in 4.4 hours. The dotted projection lines display the summed projection of the W20 sample with an offset.](image-url)
Table 4.5: Calculated EFGs and structural details of In_{0.5}Ga_{0.5}P. The configurations with $S_{CuPt} = 1$ have either all atoms fixed at ideal diamond lattice positions (“no” structural optimization, $a$ is fixed and $c/a = \sqrt{8/3} = 1.633$), have only the positions optimized (“pos”) or have both positions and cell relaxed (“pos & cell”). The $2 \times 2 \times 2$ super cell has $S_{CuPt} = 0$. The lattice constant is fixed. Ions are either fixed on ideal zincblende lattice (“fixed”), all relaxed (“relaxed”), or partially relaxed (“mix” and “mix2”, see main text). $V_{xx}$ are in $10^{20}$ V/m$^2$. Standard deviations are in parenthesis.

<table>
<thead>
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<th>structural optimization</th>
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<td></td>
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</tr>
<tr>
<td></td>
<td>1.6333</td>
<td>1.6333</td>
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<tr>
<td>$V_{in}$</td>
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<td>$8.9$</td>
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<tr>
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<td>$0$</td>
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<td>$-1.13$</td>
<td>$-10.3$</td>
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<td>2.54</td>
</tr>
<tr>
<td></td>
<td>$d(P^2\text{-In})$</td>
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<td>2.49</td>
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<td>2.45</td>
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<td></td>
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<td>106.7</td>
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<tr>
<td></td>
<td>$\angle(P^2\text{-Ga}-P^2)$</td>
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<td></td>
<td>$\angle(P^1\text{-Ga}-P^1)$</td>
<td>109.3</td>
<td>117.1</td>
</tr>
</tbody>
</table>

$^1$This is a $2 \times 2 \times 2$ cube with total edge length: $2 \times 5.6596 \times 10^{-10}$ m.

The experimental values are 6.3 and $8.2 \times 10^{20}$ V/m$^2$ respectively. It appears that the DFT models overestimate the average EFGs. A possible explanation is that the PBE-DFT functional makes small errors in describing the energetics of the subtle deformations of the tetrahedra. We have seen that the EFGs are extremely sensitive to the structure so that large changes in EFGs can easily occur. Keeping in mind this extreme sensitivity, it is conceivable that intermediate structural models exist, having both low $S_{CuPt}$ and smaller average EFGs.

In spite of these observations, we can still use calculations to learn more about the mechanisms that give rise to the EFGs. Both structural random models (“fixed” and “relaxed”) have the same lattice (dis)order, but their EFGs differ almost an order of magnitude. This means that the information on (local) ordering mainly enters indirectly into the EFGs via the structural relaxations that are characteristic of the (dis)order. With a simple model calculation we can show that the dominant structural effects occur in the first shell, i.e. the GaP$_4$ and InP$_4$ geometries determine the EFGs in leading order. Thus the first shell atoms act like an amplifier: they pick up the structural deformations resulting from the disorder and translate these into large EFGs on Ga and In.

To demonstrate this mechanism we carried out a set of calculations on model structures. We took the disordered model with all atoms at their ideal zincblende lattice positions. Then, we took
one Indium (or Ga) atom and moved only the four phosphorous atoms in its first coordination shell to their positions in the relaxed random model. The first coordination shell of the Indium atom is now exactly the same as in the relaxed model, but all relaxations in further shells are absent. We carried out a DFT calculation for the Indium EFG of this model structure, and repeated the procedure for the other 15 Indium (Ga) atoms. The result of this “mixed” model is in the column “mix” in Table 4.5. Note that the first shell accounts for most of the change in \( \langle |V_{zz}^{\text{In}}| \rangle \) and \( \langle |V_{zz}^{\text{Ga}}| \rangle \). This is even more evident when comparing the individual EFGs. Their \( V_{zz} \) are plotted in Figure 4.9.

There is little agreement between the \( V_{zz} \) of the unrelaxed (“fixed”) and relaxed structures (open diamonds) whereas the \( V_{zz} \) of the “relaxed” and “mix” model are very similar (solid diamonds). For \( V_{xx} \) we observe similar behavior (not shown). For the much smaller \( V_{yy} \) (\( |V_{zz}| \geq |V_{xx}| \geq |V_{yy}| \)) relative deviations are larger, but the model still works. The mixed model fails for the asymmetry parameter \( \eta \), as in too many data points the errors in all three \( V_{ii} \) can “add up” in a destructive manner.
Table 4.6: Standard deviations (σ) of Ga and In isotropic chemical shifts calculated for the disordered model without (“fixed”) and with (“relaxed”) structural relaxation taken into account. The FWHM is calculated as 2.34 × σ and compared to experiment. All numbers are in ppm.

<table>
<thead>
<tr>
<th></th>
<th>random supercell</th>
<th>exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>fixed</td>
<td>relaxed</td>
<td></td>
</tr>
<tr>
<td>σ</td>
<td>σ</td>
<td>FWHM</td>
</tr>
<tr>
<td>Ga</td>
<td>2.3</td>
<td>8.7</td>
</tr>
<tr>
<td>In</td>
<td>3.8</td>
<td>20</td>
</tr>
</tbody>
</table>

We tried to simplify the model even more. Instead of putting the 4 nearest neighbor atoms at the relaxed positions, we only used the relaxed bond angles. The distances were fixed to typical In-P and Ga-P distances (2.52 and 2.38 × 10⁻¹⁰ m respectively). Results are listed in column “mix2” of Table 4.5. The “mix2” model is compared to the fully relaxed model in Figure 4.9 (“+”). For Indium this works surprisingly well, i.e. only the first neighbor P-In-P bond angles are relevant (note that for $S_{CuPt}=1$ also bond distances were important). For Ga the agreement is worse, although the model still captures most of the effect.

In view of the above it is seems reasonable to assume that a Czjzek model could describe the EFG distributions. We do not have reliable statistics (note that the ⟨η⟩ are close to the ideal Czjzek average anyway), but we have seen that for a sufficiently large degree of disorder the In and Ga EFGs are determined predominantly by a distribution of four “effective charges” in the first coordination shell deviating from their ideal tetrahedral positions. Such a situation can typically be described by a Czjzek distribution. More ordered structures with lower $S_{CuPt}$ could exhibit deviations from such a distribution.

In and Ga isotropic chemical shifts were calculated for the disordered model. Table 4.6 shows the root-mean-square deviations obtained from the 16 In and 16 Ga sites, with the nuclei on the ideal zincblende lattice sites and with nuclear positions relaxed (“fixed” and “relaxed” random supercell in Table 4.5). Relaxations resulted in a significant increase of the root-mean-square deviations. The experimental trend is well reproduced.

### 4.5.2 $^{31}$P Chemical shifts

As was already discussed by Tycko and coworkers and reiterated in sec. 4.4.1 the $^{31}$P chemical shifts are a useful parameter to characterize InGaP. Not only do they allow a discrimination between the different coordinations P[Ga₁nIn₄₋ₙ] in the lattice, but also the shift values appear to increase with increasing in content $x$. The latter observation seems to contradict the fact that $^{31}$P shift in GaP (-142 ppm) and InP (-148 ppm) are very similar. Moreover, these shifts do not coincide with the measured shifts for the thin films. To elucidate this and confirm the assignments, phosphorous chemical shifts were calculated. The results are summarized in Figure 4.10.

First we consider the $^{31}$P shifts of pure InP and GaP as a function of the nearest neighbour (NN) distance ($= \sqrt{3}/4 \times$ the lattice constant). We observe that for the same NN distance, the phosphorous shifts are very different. For GaP the shift is more than 200 ppm larger (i.e. deshielded) than for
InP. In has more extended valence states as a result of which the phosphorus in InP is more strongly shielded compared to GaP. The P shift is also strongly dependent on NN distance, for both InP and GaP. It increases almost linearly and with approximately 200 ppm when going from the GaP to the InP lattice constant. The trend is consistent with chemical intuition: shielding becomes less effective when the shielding “cations” are at larger distance from phosphorous. Both effects cancel each other to a large extent, so $\Delta(\delta)$, the calculated P isotropic shift of InP at the InP lattice constant minus the calculated P shift of GaP at the GaP lattice constant is relatively small. Using the experimental lattice constants as in Figure 4.10 gives $\Delta(\delta) = -19$ ppm. Using the PBE optimized lattice constants gives $\Delta(\delta) = -7$ ppm. The experimental difference is $\Delta(\delta) = -8$ ppm.

Next we study the effect of disorder and consider the various coordinations P[GaN_{4-n}] using the disordered supercell model of In_{0.5}Ga_{0.5}P from Sect. 4.5.1. It contains 32 P nuclei. Figure 4.10(a)
Table 4.7: Calculated $^{31}$P isotropic chemical shifts in ppm compared to experiment. Random supercell: average shifts without relaxation of atoms (fixed) and with atomic positions relaxed (relaxed). $^{31}$P is referenced such that its shift is $-142$ ppm (the experimental number from Ref. [43]) for GaP at the experimental lattice constant $a = 5.4505 \times 10^{-10}$ m. [113]

<table>
<thead>
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<td>3</td>
<td>-109.2</td>
</tr>
<tr>
<td>$P[\text{Ga}_2\text{In}_2]$</td>
<td>2</td>
<td>-135.3</td>
</tr>
<tr>
<td>$P[\text{Ga}_1\text{In}_3]$</td>
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</tr>
<tr>
<td>$P[\text{In}_4]$</td>
<td>0</td>
<td>-191.2</td>
</tr>
</tbody>
</table>

shows the $^{31}$P shifts calculated with the nuclei fixed at the ideal zincblende positions, i.e. without relaxation. The calculation was done for three different lattice constants. The shifts exhibit a range of approximately 200 ppm, with the $P[\text{In}_4]$ and $P[\text{Ga}_4]$ shift being close to the shift for pure InP and GaP, respectively. For fixed $n$ the shifts just exhibit a small spread. For the NN distance of $2.45 \times 10^{-10}$ m, corresponding to the composition $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$, the averages are listed in Table 4.7 (column “fixed”). The correct ordering is reproduced, but the range of chemical shifts is much wider than experimentally observed.

Figure 4.40(b) shows that the chemical shift range due to the difference in composition in the first coordination sphere is considerably reduced when positions are allowed to relax. It is, however, still substantial, showing a difference of well over 100 ppm for the $P[\text{Ga}_4]$ coordinates compared to the $P[\text{In}_4]$ coordinates. Agreement with the experimental shifts is quite good, confirming the assignment (see Table 4.7, column “relaxed”). Relaxations also give rise to a much wider spread of shifts (within the subsets of given $P[\text{Ga}_n\text{In}_{4-n}]$-coordinates). E.g., for $n = 2$ the r.m.s. deviation increases from 1.3 to 5.6 ppm (calculated from an average of 13). These deviations help (partly) explain the relatively large line widths that are observed in the experimental NMR spectra. They are accompanied by a large spread in average NN distances.

Going from $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$ to $\text{In}_{0.86}\text{Ga}_{0.14}\text{P}$, Tycko et al. observe an increase in chemical shift of approximately 30 ppm (independent of $n$). [43] With the “fixed” model, we observe a change in shift more than a factor 2 larger, see Figure 4.40(a). However, that model does not account for (a) changes in composition away from $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$ and (b) the effect of structural relaxation. We saw in Figure 4.40(b) that the latter is substantial for $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$. We do not have structural models with other compositions to assess the effect of relaxations. However, for vanishing small Ga content, the $P[\text{Ga}_n\text{In}_{4-n}]$ with $n = 0$ should approach the P shift in pure InP. So we can compare the $P[\text{Ga}_0\text{In}_4]$ shift calculated at the $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$ and InP compositions. This gives 33 ppm, which is in the ballpark, given we have bad statistics for the $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$ model (just one P site).

4.6 Conclusions and outlook

Band gap measurements were performed for two $\text{In}_{0.418}\text{Ga}_{0.582}\text{P}$ samples grown with a pressure of 20 and 50 mbar. The energies correspond to an average CuPt LRO of 0.22 and 0.39. These order
parameters were translated to five relative occurrences of P[Ga$_n$In$_{4-n}$] sites. Using these relative intensities, the two $^{31}$P spectra could be fitted very well, putting an upper limit to the amount of order in the sample ($S < 0.5$). It proved not possible, however, to discriminate between the two samples on the basis of a difference in order parameter. Furthermore, we examined the short range ordering by analyzing the Gallium and Indium quadrupolar distributions. An quantification of the quadrupolar distribution, chemical shift distribution and dipolar coupling could be made from several MQMAS and MAS spectra at two $B_0$ fields of 9.4 and 14.1 Tesla. In the MAS and MQMAS spectra, evidence was found for a quadrupolar and chemical shift distribution. Due to the correlation between the chemical shift and the quadrupolar interaction, the MQMAS spectra could not be perfectly matched. Nevertheless, it can be concluded that the short range ordering is clearly near random.

A structural model with cationic disorder was build using DFT. From this model we found that the In and Ga EFGs are mainly determined by the deformations of the first coordination shells. Thus the effect of disorder of the higher coordination shells is indirect, as it occurs via the their impact on relaxation of atoms in the first coordination shell. Quantitative agreement with experiment could not be obtained for the EFGs. We think this might be due to insufficient accuracy of the PBE to simultaneously describe relaxations of In-P and Ga-P bonds.

The strong dependence of the $^{31}$P isotropic chemical shift on lattice constant and on chemical environment compensate each other almost perfectly. Hence, pure InP and pure GaP, having a lattice mismatch of $\sim 7\%$, exhibit nearly identical $^{31}$P chemical shifts, whereas intermediate compositions can have $^{31}$P shifts deviating substantially. The calculations on the disordered structural model, having all five P[Ga$_n$In$_{4-n}$] coordinations, showed that the relaxations away from the ideal zincblende lattice sites, nevertheless give rise to a substantial reduction of the $^{31}$P isotropic chemical shift range. This is important for obtaining good agreement with experiment. The relaxations also cause a substantial broadening of the $^{31}$P distribution for the individual P[Ga$_n$In$_{4-n}$] coordinations.

In future studies we hope to increase the accuracy of the structural modeling of (disordered) InGaP, in order to improve the accuracy of the EFGs, that typically depend very sensitively on structural detail. For the $^{31}$P chemical shift modeling larger and more models need to be considered to attain good quality chemical shift distributions. These might shed more light onto the subtle shift and line widths variations in the $^{31}$P spectra of different samples. Other compositions and order parameters also demand further study to gain understanding of the NMR response of a sample in relation to structural variations which in turn influence the electronic properties of the materials. This is a daunting computational task, however, using special quasirandom structures (Refs. [115, 116]) might help to determine more accurately the shift and $C_q$ average.

On the experimental side, being able to obtain NMR responses from single oriented films would allow a more detailed analysis of the effect of order/disorder on the NMR parameters particularly where the quadrupolar nuclei are involved. NMR spectra of single films will display the resonances of the various inequivalent sites in the unit cell. If dipolar interactions are minor (e.g. by averaging using magic angle spinning), the lines will be narrow and eventual line broadening can directly be interpreted in terms of local order or disorder that may be present. This is a great advantage over powder spectra where this information is convoluted with the orientation distribution of individual powder particles. Development of such thin film probe technology is underway.
Acknowledgements

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Chapter 5

Magnetic Resonance Force Microscopy - Introduction

In this chapter an introduction to Magnetic Resonance Force Microscopy is given. First, the functionality is described, then MRFM is compared to NMR and the race towards imaging with single nuclear spin sensitivity with MRFM is elaborated. MRFM uses a very sensitive mechanical detector, or cantilever, which can be described as an harmonic oscillator. Because the detected signals are so weak, many noise sources need to be determined, a well-considered design needs to be constructed and the signal to noise ratio needs to be considered. Detection of the MRFM signal occurs by locking the spins with radio frequent waves. The type of RF detection sweep influences the volume and shape of the resonant slice from a region within the sample. The MRFM signal depends on the force on the cantilever, originating from the spins in the slice.

5.1 The imaging of micro volumes

When a ferro-magnetic gradient is placed inside a static magnetic field, the nuclear resonant frequency of a sample becomes dependent on the position, i.e. $\omega(z) = \gamma \cdot (B_0 + \Delta B(z))$. The discovery of this relation and its implementation allowed the imaging of materials with NMR. The first MR image was published in by Lauterbur in 1973[117]. Lauterbut and Mansfield developed magnetic resonance imaging. The first person who realized that NMR images could be made of human living tissue was the American Damadian. He constructed the first prototype MRI scanner in 1972[118]. He showed that there was a difference in $T_2$ between healthy and tumor tissue. He wanted to use this for a treatment. To image smaller and smaller volumes within a human body, the SNR increased over the years. A boost in SNR was obtained by the simultaneous acquisition of phase-encoded slices, i.e. multiplexing. However, a typical spatial resolution that can be obtained with a modern MRI scanner is only about 1 mm$^3$ in a minute. A novel technique called Magnetic Resonance Force Microscopy was proposed by Sidles[23] in 1992 to image much smaller samples with a strongly
Figure 5.1: Overview of the MRFM setup, originally proposed by Sidles [23].

enhanced spatial resolution.

5.2 How does MRFM work?

In MRFM, a sample is positioned in a strong ($10^2...10^6$ T/m) gradient magnetic field. The sample is either placed on top of a cantilever or the gradient[24] is attached to the cantilever. The ensemble of nuclear magnetic dipole moments in the active, resonant slice will exert a force on the cantilever

\[ F(t) = \int_V m(t) \cdot \nabla B dV, \]  

(5.1)

with $F(t)$ the time dependent force, $V$ the volume of the sample, $m(t)$ the slice macroscopic magnetization and $\nabla B$ or $\partial B/\partial z$ or $G$ the strength of the magnetic gradient, see figure 5.1. The magnetization is modulated at the much lower cantilever eigen-frequency ($10^2...10^4$ kHz) by periodic inversions of the macroscopic $z$-magnetization using an RF waveform sequence. The most common MRFM detection procedure occurs via locking of the spins during acquisition, which are periodically inverted by Fast Adiabatic Passages (FAPs). The modulated magnetization causes a periodic displacement, which then can be detected using (for instance) an optical interferometer. The optical signal is converted to an electronic signal with photo-diodes and is detected phase-sensitive with respect to a reference frequency using a lock-in amplifier.

5.2.1 A comparison between mechanically and inductively detected NMR

The advantages and disadvantages of MRFM can be understood by comparison with NMR. The most important differences are listed and discussed here:

1. **Magnetization** In inductively detected NMR the transverse magnetization $m_x$ or $m_y$ is detected, while in the original MRFM design of Sidles, $m_z$, the longitudinal magnetization is detected. It should be mentioned here that the magnet on cantilever approach in combination with Cantilever Readout of Magnetic Inversion Transients (CERMIT) [119] can detect transversal magnetization (see Section 5.3.2). Furthermore, state of the art MRFM work detects the statistical polarization[120], hence the variance of the spin signal.

2. **Frequency** NMR directly detects at the Larmor frequency, while MRFM uses indirect detection at the cantilever eigen-frequency. Attempts are made to generate high frequency
cantilevers, for example a carbon nano-wire [121] or a short cantilevers (∼ 1 μm) operating at high frequency, for example at 128 MHz [122]. Such cantilevers are stiffer, but they can still have a low noise level, because they hardly suffer from low frequency 1/f noise.

3. Sequence Several pulse/waveform sequences have been proposed for MRFM. In general they are more of continuous wave character compared to NMR. Depending on sample relaxation properties, such as $T_{1\rho}$, $T_1$, we can choose how to periodically invert the magnetization during detection. In case of short $T_1$ for example, the magnetization can be inverted each cantilever period using short pulses. In case of long $T_1$ and $T_{1\rho}$, sweeps can be used to keep the spins locked. In this thesis, all MRFM signals were acquired via locking of the spins with FAPs. The relaxation times of all samples were longer than two seconds ($2 < T_{1\rho} < T_1$).

4. Homogeneity In NMR the $B_0$ magnetic field should be as homogeneous as possible, a typical value is <0.1 ppm. While in MRFM, effort is still undertaken to increase the magnetic gradient strength, to image with the highest possible spatial resolution. Mamim et al. reached a gradient of 1.4·10^6 T/m in 2007 and a spatial resolution of about 90 nm[123]. Degen et al. reached an extremely high gradient strength of $G = 4.2 \cdot 10^6$ T/m in 2008 and a shell thickness (FWHM) of the resonant slice of $\sqrt[2]{\Delta \omega_{r, peak}}/(\gamma \cdot G) = 4.8$ nm[120].

5. Sensitivity The sensitivity is defined as the number of spins that can be detected in a single measurement (in relation to the noise level) with a SNR of 1. The sensitivity of regular NMR is around $10^{15}$ nuclear spins. In micro coil NMR the detection limit can be reduced to roughly $10^{13}$ nuclear spins. In NMR and MRFM the enhancement of sensitivity still remains one of the major challenges. Typical spin sensitivity values of the MRFM setup in this thesis are $10^{12}$ spins at room temperature (see equation 5.27). Net spin sensitivities down to $\sim 10^2$ nuclear spins at low temperature have been reached with MRFM[123, 120, 124].

6. Detector Softer cantilevers for MRFM will improve the sensitivity, but such cantilevers will be more difficult to fabricate and require additional digital electronics[125]. Nano-wires [121] and torsional cantilevers [126] have been proposed for use in MRFM. In mechanical detection the limiting factor is normally the Brownian motion, while inductive detection suffers from Johnson noise in the resonant circuit. Sidles and Rugar derived the SNR on the basis of the coupling of the magnetic moment to a resonant electrical or mechanical circuit [127]. They find that for any resonator

$$SNR \propto \sqrt{\frac{\omega_0 Q}{k}} = \sqrt{\frac{1}{\Gamma}}$$

(5.2)

, implying that the damping factor and the spring constant should be as low as possible. Furthermore, the coupling with the spins should be as strong as possible. The mechanical resonator can perform better than the electrical resonator. Rugar and Sidles mention that the coupling factor $k$ for a mechanical detector can be much lower. The coupling factor in MRFM is given by a magnetic spring constant $k_m = k_c/\nabla B^2$. A typical MRFM system $k_c = 0.01$ N/m and $\nabla B = 1000$ T/m, yields $k_m = 10^{-8}$ J/T^2. For an inductive coupling, $k_m$ is proportional to the volume of the coil. Much higher values were reported for a coil $k_m \approx 10^{-2}$ J/T^2 [127]. In summary, the cantilever achieves a much better SNR by having a softer interaction with the magnetic moment than the coil. The ‘softness’ of the coil is achieved because of its high
\( \omega_0 \) with respect to the much lower cantilever frequency \( \omega_c \) (in the order of 100 MHz versus 10 kHz). Rugar et al. mention that an inductive coil creates and annihilates its magnetic field twice during each cycle, which entails a certain energy cost that is in proportion to the volume of the coil. A mechanical oscillator avoids this creation-annihilation energy cost. Instead, the field is moved to another location. Of course this exchanges one energy for another. The field source must still be vibrated back and forth, which requires the spending and storage of kinetic energy. However, because the cantilever is much smaller, this type of energy is much lower and this is why small cantilevers can be extremely soft and thus have very good detection capabilities [127]. The ultimate goal is to find the detector with the softest interaction with the spins and which is thus using the lowest coupling energy to excite and detect, for instance a single spin in a diamond nanocrystal [128]. Additionally, the readout and manipulation must be operating at low powers, so that the noise does not disturb the system.

5.2.2 The history of MRFM

Since the invention of MRFM in 1992 many improvements were made. Section 1.10 introduced the SNR enhancements. This section summarizes the most important historic events with regards to mostly spectroscopy and also imaging. The first MRFM image with 1 \( \mu \)m axial spatial resolution was obtained in 1993 by Zünger and Rugar at the IBM Almaden research center[129]. In 2002 Verhagen et al. measured the first quadrupolar nuclei with MRFM and described contrast imaging in MRFM[130]. The spatial resolution reached nanometer scale in 2003[24] and a huge breakthrough was the detection of a single electron spin with MRFM in 2004[131]. A mathematical description and a simulation of the quantum behavior of a single spin was developed in 2005 by Brun et al. [132]. In 2006 Degen et al. obtained MRFM data via a dipolar echo [133]. In 2007 Eberhardt and Lin et al. showed double resonance in MRFM [134, 135, 17]. In 2008 Degen et al. measured a 3D image of the structure of the tobacco mosaic virus with nanometer resolution [120]. A more detailed MRFM historic overview till 2008 is given by Kuehn et al.[119]. In 2009 a Carbon nanotube was 3D imaged with MRFM [136]. In 2011 Joss et al. showed chemical shift imaging in MRFM by moving the gradient position [137]. In 2013, the same trick was reproduced for GaAs [138]. In 2013, Tomka et al. showed capability of MRFM to image polymers (PEEK and PTFE) with such short relaxation times, using a movable gradient and a Hadamard 8 SNR enhancing scheme [139]. It should be noted here that the MRFM signal generally originates from fast spin inversions, which are often integrated to enhance signal strength. A big hurdle to overcome is to measure biological samples, because generally they have a relatively short \( T_1 \) and \( T_{1\rho} \).

In conclusion, the technique of MRFM has strongly developed over the last two decades and it has unleashed scientific progress in many other areas, like ultra-sensitive sensors, strong magnetic gradients, novel waveform sequences and mathematics for the description of the behavior of a single electron spin. The sensitivity of MRFM has increased by several orders of magnitude during the last decade, from detecting 10^{12} \(^1\)H spins to hundreds of spins [123, 120, 124]. It was achieved by altering the experimental setup, reducing noise sources, increasing gradient strength, integration of components, enhancement of the RF flux by miniaturization of the coil/strip line, adjustment of the RF/spin detection protocols and reduction of the temperature. The experimental setup was
changed by positioning the cantilever vertically and using frequency detection instead of amplitude detection (see figure 5.2). After all this research, the original idea of Sidles, to atomically image a single biological molecule with chemical contrast and single nuclear spin sensitivity, remains on the agenda.

5.3 Improved spin detection protocols

Different sequences and designs have been proposed and analyzed to progress towards the final goal of single nuclear spin sensitivity for MRFM. An impression of the experimental difficulties is given by a short description of the two important techniques that facilitate high spin sensitivity and reduction of noise sources. One of the major challenges, which became apparent when smaller forces had to be resolved, was to minimize the surface noise and its interaction with the cantilever. A waveform sequence that avoids the pickup of this undesirable noise is called Oscillating Cantilever Driven Adiabatic Reversals (OSCAR).

5.3.1 OSCAR

Modulating spins in a MRFM experiment generally requires varying the frequency or amplitude of the applied RF field. For sensitive magnetic-tipped cantilevers, these modulations can lead to a disturbing background excitation of the cantilever or drift in its resonance frequency. Therefore, it is necessary to invent a method for flipping spins that can couple to the cantilever, but avoids these troublesome effects. In the OSCAR approach to detect magnetic resonance, introduced by Stipe et al.[140], the RF power is left on continuously as the cantilever is self-oscillated via positive feedback. In an OSCAR measurement, spins are swept through resonance once per cantilever cycle by the oscillating the longitudinal field created by the moving magnetic tip of a cantilever. In this way the cyclic inversions modify the cantilever’s effective spring constant, which in turn shifts the cantilever’s spring constant

$$\Delta k_z = \frac{\partial \mu}{\partial z} \frac{\partial B_z}{\partial z} ,$$

(5.3)

this change is observed by a weak shift (typically <0.1 Hertz) in the resonance frequency of the cantilever. In this setup, the relaxation rate of the measured spins (\(\sim 1\) second) was in the order of the magnetic noise due to thermal currents in the electrically conductive tip (\(\sim 10\) seconds). A modified approach was suggested by Mamin et al.[141] to reduce the influence of this surface induced 1/f noise. In interrupted-OSCAR (iOSCAR), the spin dependent shift in cantilever frequency is
modulated at \( \pm f_c/m \) by turning off the RF every \( m \) cycles, hereby moving the spin signal to \( f_c \pm f_c/m \) away from the surface noise.

### 5.3.2 CERMIT

In many (biological and organic) samples the \( T_{1_\rho} \) is low (i.e. \(< 1 \) second). This is unfavorable for direct detection of the magnetic resonance signal, since then the spins cannot remain locked during the FAPs in the transversal plane and the MRFM SNR drops severely. However, in such cases, the CERMIT sequence offers a readout with a much better SNR [119]. This detection scheme is based on detecting the force gradient, using a waveform sequence called CERMIT. The force gradient couples the magnetic-tipped cantilever to the longitudinal component of sample magnetization, \( \mu_z \). A polarizing magnetic field is applied along the direction of the cantilever width. Sample spins are inverted using frequency-sweep adiabatic rapid passages. The inverted spins transiently shift the mechanical resonance frequency of the cantilever. If the inverted region is chosen appropriately, we detect an instantaneous resonance shift according an ensemble of spins

\[
\Delta k_z = 2 \sum_j \mu z_j \frac{\partial^2 B_z(r_j)}{\partial x^2},
\]

see ref. [142, 119]. Compared to OSCAR, the duty cycle of the RF is much lower in CERMIT, giving it an advantage at low temperature, where heating is an issue. However, the OSCAR scheme still suffered from surface noise. To this end cyclic-CERMIT, which modulated the cantilever shift at 50 Hz, was introduced by Mamin et al.[123]. Furthermore, this experiment was capable of measuring the statistical polarization, instead of the Curie-law polarization. The coherence time of the spins was, however, much lower than \( T_1 \) and \( T_{1_\rho} \). In principle, the CERMIT experiment is capable of measuring the \( T_1 \) in a single experiment.

### 5.4 The cantilever as harmonic oscillator

To understand the motion of the mechanical detector, this section explains the mechanical response of a cantilever. In figure 5.3 the cantilever is modelled as a harmonic oscillator. A displacement from the equilibrium position by \( z(t) \), will create a restoring force \( F_{spring} \), according to Hooke’s law

\[
F_{spring}(t) = -k_c z(t),
\]

with the spring constant \( k_c \). The force on the cantilever that depends on the mass of the sample \( m \) and the acceleration \( a \). A relation can be obtained with Newton’s Second law (\( F = m \cdot a \)). For a simple harmonic oscillator with no driving force and no damping

\[
m \ddot{z}(t) - k_c z(t) = 0
\]

Neglecting the mass of the cantilever, the cantilever’s eigen-frequency is \( \omega_c = \sqrt{k_c/m} \). A general solution to this differential equation is

\[
z(t) = C_1 \sin(\omega_c t) + C_2 \cos(\omega_c t) = C e^{-i\omega_c t}
\]
5.5. **Optimal Control**

![Diagram of a spring system with mass $m$, spring constant $k_c$, damping constant $\Gamma$ and an external force $F_{\text{ext}}$. The directions of $F_{\text{ext}}$ and $z$ are given by the arrows.](image)

The constants can be obtained from initial, boundary conditions. A damped, driven, harmonic oscillator has an additional damping term $\Gamma$.

$$m \ddot{z}(t) + \Gamma \dot{z}(t) + k_c z(t) = F_{\text{drive}}(t)$$  \hspace{1cm} (5.8)

The damped eigen frequency $\omega_0$ will be slightly lower than the cantilever eigen frequency.

$$\omega_0 = \sqrt{\omega_c^2 - \left(\frac{\Gamma}{2m}\right)^2} = \omega_c \sqrt{1 - \frac{1}{4Q^2}} ,$$  \hspace{1cm} (5.9)

with a quality factor $Q = \sqrt{k_c m / \Gamma}$.

When a system is driven, either by an external force, or by noise, exciting the cantilever’s Eigen-frequency, we can solve the differential equations for $F_{\text{drive}}(t) = F_0 e^{i \omega t}$. The frequency of the oscillation is the same as that of the driving force, but the oscillation can have a phase offset and the amplitude is scaled by an amount that depends on the frequency of the driving force in relation to the preferred (resonant) frequency of the oscillating system. The complex transfer function $H(i\omega)$ of a driven, damped oscillator is

$$H(i\omega) = \frac{1}{-m \omega^2 + i \Gamma \omega + k_c} = \frac{\omega_c^2}{k_c (-\omega_c^2 + i \Gamma \omega + \omega_c^2)}$$  \hspace{1cm} (5.10)

This is a Lorentzian transfer function, the phase response changes 180 degrees over the cantilever Eigen resonance [143].

### 5.5 Optimal control

An important parameter of the mechanical detection is the cantilever ring-down time. This time can be calculated with $\tau_c = 2Q / \omega_c$. In a high vacuum, the quality-factor $Q$ of a cantilever can very well exceed 10,000. In our setup a typical resonance frequency of a loaded, commercial cantilever with $k_c = 0.01$ N/m was $f_c = 1$ kHz. For such a cantilever, the ring-down time is about 3.2 seconds. For a fast response time, which is required for fast imaging and to be able to measure samples with short (< 100 ms) $T_{1p}$, it is necessary to keep the cantilever response time low (in case of the conventional detection manner of Sidles).

The cantilever response time can be shortened with the implementation of a feedback, active damping system, or optimal control. The hardware and software implementation of the optimal control is described in Ref. [3]. The interferometer signal is observed and an electronic feedback
signal is sent to a piezo located at the base of the cantilever. Typical open- and closed loop quality factors of our MRFM setup (see next chapter) are \(Q_{open} \sim 4000\) respectively \(Q_{closed} \sim 50\).

The minimum obtainable value of \(Q_{closed}\) factor was about \(~5\), which was achieved with the best possible optical alignment. The best optical alignment was reached when the angular alignment of the cantilever was iteratively optimized. When the cantilever is tilted, this causes the reflected light intensity to decrease, while the detection of an (unwanted) torsional mode might be enhanced. It should be mentioned here that under appropriate conditions of the optimal control loop, the SNR theoretically remains unaffected by the artificial lowering of the \(Q\) factor [125].

## 5.6 Thermal and interferometer noise

Because of the very weak signals in MRFM, it is important to understand a few relevant noise sources. The dominant noise source is the thermal noise of the cantilever.

### 5.6.1 Thermal noise

The average, thermal energy \(k_B T\) of a cantilever is evenly distributed over its potential \(E_{pot}\) and kinetic \(E_{kin}\) energy

\[
\begin{align*}
\langle E_{pot} \rangle &= \langle E_{kin} \rangle \\
\langle E_{pot} \rangle &= \frac{k_B T}{2} \\
\langle E_{kin} \rangle &= \frac{k_c}{2} < z^2 > ,
\end{align*}
\]

with \(k_B\) the Boltzmann constant. The thermal, white noise is causing the cantilevers vibration. Such a vibration is called 'Brownian motion'. [143] The spectral response \(S(\omega)\) can be related to the power spectral density \(S_f\), via the square of the transfer function[3].

\[
S(\omega) = H(\omega)^2 S_f = \frac{S_f \cdot \omega_c^2}{k_f^2 (\omega_c^2 - \omega^2)^2 + k_f^2 \omega^4/Q^2}
\]

And by substituting the top Equation of 5.11

\[
\frac{k_B T}{2} = \frac{k_c}{2} \int_{-\infty}^{\infty} S(\omega) d\omega = \frac{S_f Q \omega_c}{4k_c} ,
\]

an expression for the power spectral density can be derived

\[
S_f = 2\Gamma k_B T
\]

The Brownian motion is the dominant noise in the cantilever spectrum. The above equation resembles the expression for Johnson thermal voltage noise \(S_f = 4R k_B T\), in which the damping constant \(\Gamma\) is the equivalent of the resistance \(R\)[65].
5.6. THERMAL AND INTERFEROMETER NOISE

5.6.2 Interferometer noise

The readout of the cantilever vibration occurs with fiber-optic interferometry. This read-out suffers from the following three most important noise sources:

1. Laser back-action noise The number of photons \( N_0 \) that hit the cantilever, create back-action noise. Each photon transfers a momentum to the cantilever of \( 4\pi\hbar/\lambda \). By considering Poisson statistics for the number of photons \( N_0 \) hitting the cantilever the back-action power spectral density can be derived \([144]\]

\[
S_{\text{back}} = 2N_0 \left( \frac{4\pi\hbar}{\lambda} \right)^2, \tag{5.15}
\]

with \( \lambda \) the laser wavelength.

2. Shot noise of the detector The counting of the reflected photons on the photo diode is again a Poisson process. The shot noise of the interferometer detector has a force spectral noise density \( S_{\text{shot}} \)[144], which can be derived considering the noise of displacement fluctuations of the cantilever \( S_{\text{shot}}\).

\[
S_{\text{shot}} = 2N_0 \left( \frac{\lambda}{4\pi V N_0} \right)^2 \tag{5.16}
\]

The voltage noise \( S_u \) relates to the force noise via

\[
S_f = S_u \frac{k_c^2}{Q^2}, \tag{5.17}
\]

which can be used to determine

\[
S_{\text{shot}} = \left( \frac{k_c}{Q} \right)^2 S_{\text{shot}} = 2 \left( N_0 \left( \frac{\lambda}{4\pi V Q} \right)^2 \right), \tag{5.18}
\]

with \( V \) the fringe visibility, defined in Equation 6.5.

3. Thermal noise of the photo detector The thermal noise of the detector, is caused by the dark current leakage through the photodiode, which is amplified by an operational amplifier.

\[
S_{\text{therm}} = \left( \frac{k_c}{Q} \right)^2 \frac{4k_B T}{R} \left( \frac{\lambda}{4\pi I_0 V C_{pb}} \right)^2, \tag{5.19}
\]

with the resistance \( R \) and \( C_{pd} \) the photo-diode conversion factor. In practise, for all values of \( I \) and \( R \), it was generally lower than the shot noise and back-action noise and this term can be neglected. It can become relevant for more sensitive cantilevers, with higher \( Q \) factors and a lower spring constant. The detector thermal noise was observed in the cantilever spectrum as a baseline (see also Equation 7.1, term B). In the cantilever spectrum, the thermal noise contribution was frequency independent (see ref. [3]) and was best visible at frequencies above \( \sim 5 \text{ kHz} \).

Since the number of photons \( N_0 \) is linearly proportional to the applied laser power, an optimum laser power can be derived on the basis of the first two dominant noise sources of the detection. The optimum laser power is then

\[
P_{\text{opt}} = \frac{c\lambda k_c}{8\pi V Q} \tag{5.20}
\]
At this power, the contribution from shot and back-action noise is

\[ S_{\text{shot+back}} = \frac{4\hbar k_c}{V Q} \]  

(5.21)

Typical values were a fringe visibility of \( V = 0.2 \), \( Q_{\text{closed}} = 10 \) and \( P_{\text{opt}} = 1 \mu W \). The forward laser power is then \( P_{\text{forward}} = 50 \mu W \), based on 4% reflection from the cantilever and a 50/50 bi-directional coupler.
5.7 Signal to Noise Ratio

Knowing the optimal working conditions for this sensitive, mechanical detector with optical readout, it remains to investigate the signal to noise ratio. The minimal detectable force $F_{\min}$ of the open or closed loop cantilever, in a single acquisition, is

$$F_{\min} = \sqrt{2S_f b_w} = \sqrt{4\Gamma k_b T b_w},$$

with a measurement bandwidth $b_w$ [145]. The force signal to noise ratio is

$$\text{SNR}_{\text{force}} = \frac{F_{\text{slice}}}{F_{\min}} = \frac{M_{\text{slice}} \frac{\partial B}{\partial z}}{F_{\min}},$$

with $M_{\text{slice}}$ the magnetization within the resonant slice. The strength of the magnetization depends on the number of resonant spins $n$ and can be derived from the Curie magnetization, see Eq. 1.10. We rewrite Eq. 5.23 into

$$\text{SNR}_{\text{force}} = \frac{n\gamma^2 \hbar^2 I(I+1)B_0}{3k_b T} \frac{\frac{\partial B}{\partial z}}{\sqrt{4\Gamma k_b T b_w}},$$

At low gradient field strength it is possible to set the detection slice width to the entire sample volume. The minimal number of spins $N_{\min}$ that can be detected in 1 scan with a SNR of 1 is then

$$N_{\min} = \frac{3k_b T \sqrt{4\Gamma k_b T b_w}}{\gamma^2 \hbar^2 I(I+1)B_0 \frac{\partial B}{\partial z}}.$$

The spatial resolution of the imaging system is $\gamma \frac{\partial B}{\partial z}/(2\pi)$ and the slice height $\Delta z$ depends on the excited, effective slice width $\Delta \nu_{\text{eff}}$

$$\Delta z = \frac{\Delta \nu_{\text{eff}}}{\text{resolution}} = \frac{2\pi \Delta \nu_{\text{eff}}}{\gamma \frac{\partial B}{\partial z}}.$$

Filling Equation 5.25 in Equation 5.24 and assuming the sample is a perfect cube, we can substitute in the slice height $\Delta z$ [146]

$$\text{SNR}_{\text{force}} = \frac{N_a \gamma^2 \hbar^2 I(I+1)B_0}{3k_b T} \frac{\frac{\partial B}{\partial z}}{\sqrt{4\Gamma k_b T b_w}} \cdot \frac{\Delta \nu_{\text{eff}}}{\text{sample}(3,4)} \cdot \frac{\Delta \nu_{\text{eff}}}{\text{field}(5)} \cdot \sqrt{\frac{T}{\Gamma}},$$

with $\nu_H$ the proton Larmor frequency, $\rho$ the density of mass of the sample ($m=\rho V$), A the lateral cross-section area of the slice and $\Delta \nu_{\text{eff}}$ the effective slice width. $T_{\text{lim}}$ is the limiting time constant in an MRFM measurement. Here we will discuss the options to maximize the various terms.

1. **Frequency** For maximum SNR, increase the Larmor frequency $\nu_H$. Increasing the Larmor frequency or $B_0$ is rather expensive due to the large, super conducting magnet.

2. **Temperature** Decreasing the temperature offers a more interesting option, since the SNR $\propto T^{-3/2}$. Many MRFM experiments take place at low temperatures [123, 131], offering strong signal enhancements in comparison with room temperature. However, this can limit sample choice and generally increases the $T_1$. 


3. **Number of spins** The increase of $\rho$, $\rho_{spin}$ and the sample slice area $A$ is favorable, simply because there will be more spins.

4. **Detection bandwidth** The lock-in integration time $\tau_L$ should be set with care. It is not recommended to set $\tau_L >> T_{1P}$, since this will filter the MRFM signal and signal intensity will be lost during the long build-up. If needed, additional filtering can always be applied after the acquisition. It is not recommended to set $\tau_L << T_{1P}$, since the SNR will decrease proportionally to $\sqrt{\tau_L}$. $T_{lim}$ is then defined by the effective integration time of the lock-in, which can be calculated with Ref. [145]. The bandwidth of the lock-in amplifier should be set slightly higher than the signal bandwidth, or the lock-in integration time should be set slightly lower than the effective relaxation of the MRFM signal, i.e. $\tau_L \leq T_{1P}$.

5. **Effective field** If our $B_1$ field is strong enough, we can enhance our SNR by periodically inverting more spins adiabatically during the detection period. This becomes more important at strong gradient fields, since the MRFM signal extends over a broader frequency range. In case of triangular sweep detection, $\Delta \nu_{eff}$ equals 0.808 times the full sweep amplitude [65]. The maximum slice height (and SNR) is obtained by setting $\Delta \nu_{eff}$ maximal but the detection should still be adiabatic.

6. **Cantilever damping constant** The cantilever should have the lowest possible damping constant, however the handling of such cantilevers is tedious. Mounting the sample and placing it in the setup will become a very difficult task. Huge progress in making cantilevers more sensitive has been made over the last decade [121, 122, 147]. High (Larmor) frequency cantilevers can still be relatively soft.

### 5.8 The Fast Adiabatic Passage

During the detection phase of the MRFM acquisition the macroscopic magnetization is periodically inverted with the cantilever eigen frequency. For long $T_1$ and $T_{1P}$ the spins should remain locked and the inversion can be done with Fast Adiabatic Passages (FAPs), see figure 5.4. Imagine a reference frame, rotating at exactly the irradiation frequency $\omega(t)$. The effective magnetic field $B_{eff}$ can now be visualized as a vector sum of the off-resonance frequency

$$\Omega(t) = \omega(t) - \omega_0$$  \hspace{1cm} (5.28)

and $\omega_1$, the RF field strength. The magnitude of the effective magnetic field is $B_{eff} = \sqrt{B_1^2 + (\Delta B_z)^2}$, with $\Delta B_z = \gamma \Omega$. The variation of the angle with respect to $B_0$ can be written as

$$\theta(t) = \arctan\left(\frac{\Omega(t)}{\omega_1}\right)$$  \hspace{1cm} (5.29)

To describe the efficiency of the adiabatic passage, we introduce an adiabaticity parameter $A$, which can quantify the adiabatic condition [3, 65]

$$A(t) = \frac{\omega_{eff}(t)}{\theta(t)} \underset{\text{on-resonance}}{=} \frac{\omega^2(t)}{\Omega} ,$$  \hspace{1cm} (5.30)
with $\omega_{eff} = \gamma B_{eff}$. For linear sweeps, the lowest, critical value of the adiabaticity is obtained at the on-resonance frequency. A full adiabatic inversion maintains signal intensity and coherence of the spin system. For an adiabaticity $A < 1$, the transition is sudden and the signal intensity is reduced, while $A > 1$ denotes adiabatic transfer. A practical requirement was $A > 5$. An important parameter for MRFM detection using FAPs, is the effective decay time of the spin-locked magnetization in the rotating frame $T_{1p}^*$:

$$\frac{1}{T_{1p}^*} = \frac{1}{T_1} \left( \frac{\Omega^2}{\omega_{eff}^2} \right) + \frac{1}{T_{1p}} \left( \frac{\omega_{eff}^2}{\omega_{eff}^2} \right)$$

(5.31)

It depends on two sample parameters $T_1$ (longitudinal relaxation) and $T_{1p}$ (relaxation in the rotating frame)[148]. Increasing the off-resonance frequency $\Omega$ is favorable since $T_1 > T_{1p}$.

## 5.9 Point Spread Function

As shortly mentioned in Section 5.7, the effective bandwidth $\Delta\nu_{eff}$ (and the height) of the detected slice is less than the full bandwidth of periodic sweeps. The effective bandwidth can be calculated by considering the Point Spread Function (PSF). Ideally, this function is a step function with the frequency width equal to the corresponding slice height. In practice, the PSF, $s(\Omega)$, describes the contribution of the spins at any offset frequency $\Omega$. The derivation of this equation is insightful and was discussed in Ref. [65].

Let us assume a 100% adiabatic, periodic magnetization inversion with no relaxation during all the FAPs. The effective macroscopic magnetization will exactly follow the applied $B_{eff}$ field and the time dependent force exerted on the cantilever is

$$F(t) = \frac{1}{\gamma} \int_{-\infty}^{\infty} M_z(\omega_0) \cos(\theta(\Omega, t)) d\omega_0$$

(5.32)

$M_z(\omega)$ is the longitudinal starting magnetization before the detection with the FAPs. $\theta(\Omega, t)$ now considers the frequency $\Delta\omega_{rf}(t)$ modulation of the applied detection waveform and a possible amplitude modulation $\omega_1(t)$. For each offset frequency $\Omega$

$$\cos(\theta(\Omega, t)) = \frac{\Delta\omega_{rf}(t) - \Omega}{\sqrt{\omega_1(t)^2 + (\Delta\omega_{rf}(t) - \Omega)^2}}$$

(5.33)

During the detection period, the lock-in amplifier integrates the voltage/force at the cantilever resonance frequency over time. Thus, the driving force $F_0$ is measured at the first harmonic frequency.
\[ f_c \]

\[
F_0 = \frac{1}{\gamma} \int_{-\infty}^{\infty} d\omega_0 M_z(\omega_0) \frac{4}{T_c} \int_{-T_c/4}^{T_c/4} dt \sin(2\pi t/T_c) \cos(\theta(\Omega, t)) = \frac{1}{\gamma} M_z(\omega_0) * s(\Omega) , \tag{5.34}
\]

with \( T_c = 1/f_c \), the inverse cantilever frequency. The MRFM spatial signal is a convolution of the magnetization from the nuclear spins in the slice with the applied, detection PSF. The PSF, \( s(\Omega) \), depends on the detection waveform.

A "rectangular", narrow PSF is desirable, since it directly relates the MRFM signal intensity to the magnetization and the corresponding number of spins in each slice. The inverse Fourier transform of a rectangular function is a 'sinc' function. Such a detection profile unfortunately generates a very strong cantilever noise. A convenient, realistic, detection profile, which modulates the spins at the cantilever eigen-frequency, is the triangular sweep. For a triangular wave detection function with constant amplitude \( \omega_1(t) = \omega_1 \) and \( \Delta \omega_{rf}(t) = 2\Delta \omega t/T_c \), \( \Delta \omega \) is the half amplitude of the detection sweep, we obtain

\[
s(\Omega) = \frac{4}{T_c} \int_{-T_c/4}^{T_c/4} dt \sin(2\pi t/T_c) \frac{2\Delta \omega t/T_c - \Omega}{\sqrt{\omega_1^2 + (2\Delta \omega t/T_c - \Omega)^2}} \tag{5.35}
\]

\[
\approx \begin{cases} 
\frac{4}{\pi} (1 - \frac{\omega_1}{\Delta \omega}) \cos(\frac{\Delta \Omega}{2\Delta \omega}) & \text{if } |\Omega| < \Delta \omega/2 \\
0 & \text{otherwise}
\end{cases}
\]

in the last step we assumed \( \Delta \omega >> \omega_1 \). An effective slice width \( \Delta \omega_{eff} \) is given by a rectangular function which has a similar area as \( s(\Omega) \)

\[
\Delta \omega_{eff} = \frac{\int d\Omega s(\Omega) \Omega}{\int ds(\Omega)} \tag{5.36}
\]

For a linear sweep with frequency modulation \( \pm \Delta \omega/2 \), \( \Delta \omega_{eff} \approx 0.8 \Delta \omega \) [65]. Section 9.4.2 shows that the PSF can be determined with an MRFM measurement.
5.10. The MRFM signal

A sensitive detection of a weak voltage oscillating at an audio resonance frequency is feasible with a lock-in amplifier. The lock-in amplifier allows narrow band, phase sensitive detection. In most cases, the actively damped cantilever response time \( \tau_c << T_{1p}, \tau_L \) and the integration time of the lock-in amplifier determines the build-up of the MRFM signal, while the sample \( T_{1p}^* \) determines the exponential decay (see figure 5.5). The signal transient in frequency domain \( Y(\omega) \) can be written as a convolution of the force signal \( F(\omega) \) with \( H_C(\omega) \), the cantilever transfer function and \( H_L(\omega) \), the lock-in transfer function

\[
\begin{align*}
H_L(\omega) &= \frac{1/\tau_L}{i(\omega - \omega_0) + 1/\tau_L} \\
H_c(\omega) &= \frac{\omega_c^2/k_c}{(\omega + \omega_0 - i/\tau_L)(\omega - \omega_0 - i/\tau_c)} \\
F(\omega) &= \frac{F_0\delta(\omega_0 - \omega)}{i(\omega - \omega_0) + 1/T_{1p}} \\
Y(\omega) &= H_L(\omega) H_C(\omega) F(\omega)
\end{align*}
\]

(5.37)

with the common modulation frequency \( \omega_0 = \omega_c \cdot \sqrt{1 - 1/(4Q^2)} \). The time domain signal \( y(t) \) is given by the inverse Fourier transform of \( Y(\omega) \).

\[
y(t) \sim \frac{F_0\omega_c Q T_{1p}}{k_c \omega_0} \left[ e^{-t/T_{1p}} - e^{-t/\tau_L} \right] \frac{T_{1p} - \tau_L}{T_{1p} \tau_L}
\]

(5.38)

Figure 5.5: \(^1\)H averaged and fitted MRFM signal from 4 acquisitions of an \((NH_4)_2SO_4\) sample, the fitted \( T_{1p} = 2.5 \, s, \tau_L = 1 \, s \), the frequency was 185.4 MHz. The slow build-up is due to the long lock-in integration time. The decay is due to the loss of locked spins over time, within the slice.
Normally, the absolute value of the signal is of interest and the MRFM signal can be integrated, which yields an expression for the absolute driving force [149]

\[ Y_{\text{int}} = \int_{-\infty}^{\infty} Y(\omega) d\omega \]

\[ |F_0| = |Y_{\text{int}}| \frac{k_c}{QT_1 \rho} = \frac{|U_{\text{int}}|}{S} \frac{k_c}{QT_1 \rho} \],

(5.39)

where \(U_{\text{int}}\) is the integrated voltage. This equation can be used to relate the integrated voltage to the driving force \(F_0\) and to the corresponding number of spins.
Chapter 6

MRFM experimental design

This chapter contains the design issues of our MRFM setups. We first describe three MRFM designs. The design of the optics and RF wave generation is further elaborated in the following sections.

6.1 MRFM probe design

Three MRFM setups are described in figure 6.1. They are based on the original design proposed by Sidles in 1992 [23]. The aim of these designs is to image a micro volume, approximately 50×50×50 μm, with relatively spin sensitivity of about 10^{12} spins at room temperature. One MRFM probe is constructed by Verhagen et al. [3] In this thesis we refer to this MRFM probe as ‘design I’. Although MRFM design I (figure 6.2) has the possibility to adjust the magnetic gradient strength by moving the gradient piezo, a main short-coming of this probe is its stability. The gradient can drift a few micrometers in a day. If the cantilever stage is not mounted properly, the cantilever drifts away from the laser spot and the MRFM experiment needs to be stopped. In this situation, the vacuum is released, the probe is dismounted, the gradient removed and the laser spot re-aligned. To address the issues, design IIa is proposed. This design is mainly focused on increasing stability. Furthermore, the magnetic gradient field and the RF field strength are increased. Therefore, the spatial resolution is increased and the adiabatic condition is less stringent. During assemblation of the probe it is noticed that the large gradient causes too much electro-static interaction with the cantilever. Besides this, the optical alignment with the lens is extremely time consuming. Finally, design IIa is modified to design IIb, by placing a long cylindrical gradient with a diameter of ~180 μm beneath the cantilever. The scaled, mechanical design IIb is displayed in figure 6.4.
**Figure 6.1:** Schematic representation of the three designs (not to scale). The arrows indicate the possible movement direction of the piezo’s. (a) The design of the available probe [3]. The position of the gradient, cantilever and fiber has to be aligned manually. The fiber piezo is used for drift control and the cantilever piezo for the optimal control. (b) Initial re-design. The laser spot is focused with a lens on cantilever. The position of the strip line, gradient and optics are fixed. The z-piezo of the Atto-cube stack is used for drift control. The attocubes can be used for in situ x,y,z alignment. The inverted gradient cone generates a maximum gradient magnetic field. (c) The adapted design of IIa. A much smaller gradient is placed in close proximity of the fiber.

* The "attocube" stack consists of ANP50 51 and ANP50 AttoFLEX x, y and z slib-stick piezo’s from the company "attocube systems" mounted on top of each other. The slib-stick piezos are currently often used in nano-applications for their relatively long travel (4 mm) but small step size (25 nm) at room temperature.

**Figure 6.2:** (left) Photograph of probe design I. (right) New probe design IIa.
Figure 6.3: (left) Photo of the constructed, new MRFM probe, design IIa/b. (right) Top-view of the Atto-cubes with strip line and RF leads. The cantilever and the camera are not mounted.
Figure 6.4: Design IIb. (Upper left) Top view. (others) Projected side views. The positions of the cantilever, the Atto-cubes, the strip line, the fiber and the buried gradient are displayed.
Table 6.1: MRFM probe characteristics, the typical to optimal values are indicated by three dots. The signal bandwidth is calculated on the basis of the typical values for the RF field, the magnetic gradient, the Q factor and the mass, here labeled as: A, B, C and D. $T_{lock} = 1$s. The spin detection limit is calculated using Eq. 5.25, assuming a detection over the entire signal bandwidth with sufficient adiabaticity.

* typical RF power required to lock the spins. The maximum, limiting power is determined by the limit when the spin temperature cycling does not function, because the RF heating is changing over time. This is the first effect that is noticed when the RF power increases. Applying even more RF power can make the cantilever drift away from the optical alignment at the beginning of the measurement. This can destabilize the optimal control during any time of the measurement.
** transversal separation from center of the sample to the coil $\Delta x \approx 100 \, \mu m$.
*** see Section 6.3.
**** The height of the strip line was 100 $\mu m$, an maximum sample height was assumed here of $\approx 20 \mu m$ and a workable separation distance of 20 $\mu m$.
† $B_0 = 4.3$ Tesla.
⊙ the mass density of ammonium sulfate was used $\rho = 1.769 \, g/cm^3$.

An overview of the MRFM probe characteristics is given in table 6.1. The use of a special RF element, a so called 'strip line' (see Section 6.3), instead of the micro coil, in combination with a stronger magnetic gradient, a more sensitive cantilever and smaller samples can increase the spin detection limit by a factor of $\approx 300$.

### 6.1. Other noise sources

Apart from the thermal and interferometer noise discussed in Section 5.6, the following noise sources need to be considered.

- **Heating.** The RF power from the micro-coil is the strongest heat source in the design. Heating can cause drift of the alignment between the optics, the cantilever and the gradient. In addition, heating can change NMR parameters, such as $T_1$, causing the measurement to not...
be reproducible when long term signal averaging is needed. In practice this meant that the continuous wave RF power during an MRFM measurement, in the micro-coil setup of MRFM design I, is kept below 3 Watt. However, it depends on the MRFM design and configuration how much the RF heating affects the alignment and the $T_1$ of the sample.

- **Vibrations.** To isolate vibrations, the probe and optical table are placed on a separate concrete slab. Low frequency oscillations can be transmitted over long distances. This turns out to be a big problem. In the surroundings of the NMR building, new buildings are constructed. This causes a lot of noise, which is picked up by the extremely sensitive mechanical detector. The noise profile is unpredictable, varying over time and in strength during the rather long (i.e. hours) MRFM measurement. To this end, a monitor function is build in to maintain the standard deviation of the vibration amplitude below 0.5 nm per second. The vacuum pump causes a significant amount of vibrations and is placed >3 meters from the setup on a different concrete slab. The increased distance increases the pumping time needed to reach a high vacuum ($<10^{-6}$ mbar). A heavy box of sand is used to dampen the vibrational standing waves in the vacuum pump, which are conducted towards the MRFM probe.

- **Electrical noise.** Electrical noise can be induced via net power fluctuations or ground loop issues, they can be picked up inductively. The grounding of the probe/cantilever does not have a strong effect in MRFM design II, which uses twisted pair cabling. However, grounding is required in design I, which has many loose wires that work as antennas, hereby inductively picking up voltage glitches. In both designs, strong 50 Hz and 200 Hz frequency components are visible in the cantilever spectrum, despite the low pass ($<50$ Hz) filtering in the electronics.

- **Air flow.** The laser and free-space optics are shielded from the outside using a closed black box, hereby suppressing air flow and external stray light. Air flow is known to influence these sensitive interferometers.

- **Laser noise.** This is an important noise source. The fiber-end is periodically moved by applying a triangular voltage function onto the fiber piezo (see figure 6.5). The forward and the reflected laser power $R$ and $F$ are monitored with a photodiode. The electrical signals from both photodiodes are amplified with operational amplifiers (opamps). Furthermore, the voltage from the forward branch, is amplified by an additional factor $n = 0...1$. This factor $n$ is manually adjustable with a potentiometer. With the potentiometer, the voltage from the two branches can be brought in balance so that the signal $R - n \cdot F$ is 0 on average. In this manner, the $1/f$ laser amplitude noise is significantly reduced. Remaining $1/f$ laser phase noise is visible in the cantilever resonance spectrum, see Equation 7.1 and Section 6.2.6. This is the strongest noise term, determining the detection limit at low frequencies. The fiber connections and the transitions from fiber to air can also pick up small vibrations and are isolated from air flow and vibrations. The laser phase noise is converted via the interferometer into amplitude noise. The laser phase noise scales with the coherence length of the laser. Because only the amplitude is measured with the photodiodes and not the phase of this signal (as is done for example in NMR with quadrature detection), phase noise can not be averaged out like amplitude noise.


**Figure 6.5:** Simulation of the reduction of laser amplitude noise in the reflected signal branch.

Laser phase noise in interferometer setups can be reduced by the following two possible solutions. The first one is to have exactly identical path lengths for the reflected and signal branch. In this manner the phase of the forward and reflected laser power have a direct relation with the amplitude of the signal and phase noise is subtracted. The difficulty here is that the lengths have to be exactly equal, with absolute fiber lengths of meters and optical path differences of only nanometers ($\lambda \equiv 670$ nm). The second option is quadrature detection. By knowing the two phases of the photodiode signals and knowing the optical length differences of the fibers the phase noise can be averaged out. Here it is important that the two sensors have the same amplification and integration constants, since this can affect the response time and the measured phase. In practice the reflected branch needs a higher amplification than the forward branch.

- **Electro-static noise.** The electro-static surface interaction from a big (conducting) surface can generate spurious noise on the cantilever, hereby reducing the $Q$-factor of the cantilever. The electro-static noise can be reduced by grounding the cantilever and the Atto-cube piezo’s (see figure 6.6). The electro-static interactions severely limit the working distance and thus the maximal gradient strength (only $\sim 100$ T/m). A gradient with a big surface, in close proximity to the cantilever should be avoided or shielded. This noise is attributed to the attraction or repulsion of charge from the iron gradient with the cantilever. The cantilever can not be fully grounded, since a conducting layer on the cantilever would create problems for the application of the RF power. The presence of these spurious noise forces is also observed with the smaller, cylindrical gradient with a diameter of 300 $\mu$m, although this gradient can be positioned at closer distances. For more than $\sim 100$ $\mu$m distance, the repelling charges generate a more or less average force on the cantilever. By applying a constant DC voltage difference over the cantilever and gradient this effect can be compensated. A similar feedback procedure is used in Electrostatic Force Microscopy. Below the $\sim 100$ $\mu$m the electrostatic noise can no longer be compensated with a constant DC voltage.
**Figure 6.6:** (left) Electro-static influence of an iron gradient with a diameter of ~ 3mm with a cylindrical hole of 300 μm, in close proximity of the cantilever. The ‘not grounded’ data-points at 200 and 400 μm separation suffered from a strong spurious noise destroying the resonance of the cantilever at the eigen-frequency. The Q factors below 5,000 had a worse detection limit ≥ 2 pm^2/Hz. With this detection limit it becomes more difficult to tune the optimal control. The cantilever resonance frequencies ranged from 700...7000 Hz. The dotted line is a guide for the eye. (right) The setup that was used to obtain this data.

### 6.2 Optical design

In general, there are several methods for reading out a cantilever vibration. Examples of existing methods with the capability to measure height differences with sub-picometer resolution in a high vacuum and a high magnetic field are

- **Tuning forks.** Tuning forks have been used in the past in AFM [150, 151]. The most successful tuning forks are the quartz tuning forks. Their operation is based on the piezo-electric effect. The cantilever is attached to one leg of the tuning fork, transferring the vibrations from the cantilever to the tuning fork. Tuning forks are appealing because of their high quality factor, but their high stiffness can be a drawback for use in MRFM at low frequencies. Other disadvantages of the use of a tuning fork for MRFM can be Eddy currents due to the strong magnetic field, the complex feedback and a questionable resolution. Giessibl et al. [150] report a spectral noise density of 0.17 pm/√Hz at room temperature, for a 25.8 kHz Eigen frequency.

- **Capacitive readout.** The capacitive resonator readout of a cantilever is mentioned by Pelekhov et al. [152]. They show that such a readout is possible in MRFM. In their setup, the cantilever is capacitively coupled to a 2.5 GHz microwave sensing resonator. With this resonator they achieve a readout sensitivity of around 5 pm/√Hz at room temperature. A disadvantage is the electro-magnetic radiation. The RF that is used in the detection could interfere with the MRFM measurement.
• **Piezo-resistive readout.** The fabrication of ultra-sensitive piezo-resistive cantilevers is described by Jiang et al. [153]. The application of piezo-resistive cantilevers in MRFM is shown by Volodin et al. [154]. The construction of cantilevers with a low spring constant is challenging by itself. A disadvantage is that the incorporation of piezo-resistivity in the cantilever will affect the cantilever properties. This can limit for example the lower range of spring constants.

• **Laser triangulation.** In this detector, a laser spot reflects from the cantilever surface to a (four quadrant) Position Sensitive Detector (PSD). Laser triangulation is a well-known technique, which is regularly used in AFM. It has been demonstrated to function properly in MRFM [17]. Disadvantages of the laser triangulation are that the optics in the probe occupy a lot of space close to the cantilever. The optical pathway in the probe needs to be non-magnetic, although the optical components should be fixed with μm accuracies. Accurate positioning mechanics are required. It is necessary that these mechanics can be operated from outside of the magnet, since the position will vary when the probe is inserted into the magnetic field. The sensitivity is comparable to interferometry.

• **Fiber-optic laser interferometry.** An overview of the interferometry is given in figure 6.7. A laser beam is coupled into a single mode fiber. In the fiber, the light is split in a 2x2 bidirectional coupler. One forward branch of the fiber coupler is directly connected to a forward photo diode. This photo diode monitors the amplitude of the laser power, which can be used for laser amplitude noise compensation. The other branch ends close to the cantilever. A change in cantilever position changes the phase of the reflected optical signal in the branch. The optical signal, reflected from the surface of the fiber, interferes with the reflected signal from the cantilever. The reflected photo diode detects an interference pattern, which can be used to monitor the cantilever displacement [155].

Here we mention three main design advantages why 'fiber-optic laser interferometry' is a preferable choice. First, most of the optical setup can be placed outside the magnetic field on an optical table. Only the fiber needs to be close to the cantilever. There is no need for sophisticated mechanics and electronics inside the probe head. Second, a possibility exists to use external thermal control of the laser wavelength. This allows feedback outside of the magnet, omitting the need for an additional drift-compensating piezo near the fiber-end, where the detection occurs [156]. Finally, a calibration for the cantilever vibrational scale can easily be performed by making use of the laser’s wavelength. A practical disadvantage is the close proximity of the fiber to the cantilever and the fiber-end can get damaged or dirty. The working distance can be increased with a lens.

To summarize, the signal to noise ratio of the detector should be maximized by considering the signal sensitivity and the spectral noise density of the system. Furthermore, the sensor has to work under these rather extreme conditions and any source of undesired coupling into the detection mechanism should be minimized. This means that dissipation of the detector should be kept to a minimum. The detector should be capable of detecting a signal in the low frequency range of 300...7000 kHz. The decision is made to use fiber-optic laser interferometry for detection.
6.2.1 The cantilever as a thin film, Fabry Perot etalon

In this Section the total reflection of the cantilever in air is derived. The thin film cantilever can be considered a Fabry Perot etalon. An incoming ray has multiple reflections within the cantilever. Here, we consider the rays under a perpendicular angle, the angular incidence in figure 6.8 is only for convenient display.

\[
E_{1r} = E_0 r e^{i\omega t} \\
E_{2r} = E_0 t' e^{i(\omega t - \delta)} \\
E_{3r} = E_0 t'^3 e^{i(\omega t - 2\delta)} \\
E_{nr} = E_0 t'^{2n-3} e^{i(\omega t - (n-1)\delta)} \\
E_r = \sum_{n=1}^{\infty} E_{nr}
\]

(6.1)

in which \( \delta \) the optical phase difference between the rays, \( r \) the reflection and \( t \) the transmission coefficient (see Ref. [157]). The prime indicates the direction of the wave. By neglecting the optical absorption, we can use the relations \( r = -r' \) and \( tt' = 1 - r^2 \). The resultant reflected scalar wave

\[E_r = \sum_{n=1}^{\infty} E_{nr},\]
6.2. **OPTICAL DESIGN**

![Graph](image)

**Figure 6.9:** Wavelength dependence of the reflectance of the cantilever due to interference effects. \(d=600\text{nm}\) and \(n_{cl}=2.0\), resulting in \(R_{cl} \approx 34.5\%\). The laser was operating at a wavelength of 670 nm.

\(E_r\) converges if the series approaches infinity.

\[
E_r = E_0 e^{i\omega t} r \left( 1 - e^{-i\delta} \right) \frac{1}{1 - r^2 e^{-i\delta}}.
\] (6.2)

The reflected intensity is \(I_r = E_r E_r^* / 2\)

\[
I_r = I_i \frac{2r^2(1 - \cos(\delta))}{1 + r^4 - 2r^2 \cos(\delta)}.
\] (6.3)

with \(I_i\) the incident intensity \(I_i = E_0^2 / 2\). We can now write the total reflectance of the cantilever \(R = rr'\) as

\[
R_{cl}(\delta) = \frac{2R(1 - \cos(\delta))}{1 + R^2 - 2R \cos(\delta)}.
\] (6.4)

This result was also obtained in [158].

The thickness of the cantilever \(d = 600\) nm, which is of the same order as the laser wavelength \(\lambda = 670\) nm, thus it is important to consider interference within this thin film. The refractive index of the Silicium Nitride cantilever is \(n_{cl} = 2.0\). The surface reflection in air under normal incidence is relatively low. \(R = (n_{air} - n_{cl})^2 / (n_{air} + n_{cl})^2 = 11.1\%\). The optical phase difference \(\delta = n_{cl} 2d \cdot 2\pi / \lambda \approx 22.5\) radians \(\approx 3.6\) wavelength periods. The wavelength dependency of \(R_{cl}(\delta)\) is plotted in figure 6.9. The total reflectance of the cantilever at 670 nm is around 34.5%.

6.2.2 **Two beam approximation of the cantilever reflection at the fiber-end**

Now we include the cavity of air between the output of the fiber and the cantilever surface and derive an equation for reflection of the cantilever at the fiber-end. Unlike the multiple reflection model for the rays inside the perfect slab of the cantilever, now we choose a dual beam model. This is because the fiber-end has an even lower reflection constant of about 4%, furthermore, the two surfaces will not be aligned as perfectly parallel as in the thin film. Let us first consider the general case of two
interfering waves $E_{1r}$ and $E_{2r}$ due to the reflection of $E_0$ under normal incidence on two parallel surfaces, see figure 6.10.

A photodiode measuring the total reflected intensity will have the following dependency on the optical phase difference $\delta$

$$I = < E_{1r} >^2 + < E_{2r} >^2 + 2 < E_{1r} E_{2r} >$$

$$= A_1^2 + A_2^2 + 2A_1A_2 \cos(\delta)$$

$$= A_0^2[R_f + (1 - R_f)^2 R_{cl} + 2\sqrt{R_f R_{cl}}(1 - R_f) \cos(\delta)]$$

$$= A_0^2[R_f + (1 - R_f)^2 R_{cl} + V \cos(\delta)] \quad (6.5)$$

where $<>$ denotes the time integration performed by the photo detector, $V = 2\sqrt{R_f R_{cl}}(1 - R_f)$ the fringe visibility, $R_f$ the fiber to air reflectivity and $\delta = 2 \cdot x \cdot 2\pi/\lambda$, with $x$ the fiber to cantilever separation. From the photo diode intensity, it is possible to determine the relative position within $\Delta x = \pm \lambda/8$. A fiber-piezo feedback keeps the optimal sensitivity around the center of a fringe. The fiber to air reflectivity can be calculated with

$$R_f = \frac{\left(n_{air} - n_{fib}\right)^2}{\left(n_{air} + n_{fib}\right)^2} \quad (6.6)$$

For $n_{fib} = 1.47$, $R_f = 3.6\%$. Maximum amplitude modulation or sensitivity can be achieved at a theoretical distance separation of 0 $\mu$m and the theoretically maximum fringe visibility $V \approx 21.5\%$. The contrast is defined as

$$\text{contrast} = \frac{I_{max} - I_{min}}{I_{max} + I_{min}} = \frac{V}{R_f + (1 - R_f)^2 R_{cl}} = \frac{2\sqrt{R_f R_{cl}}(1 - R_f)}{R_f + (1 - R_f)^2 R_{cl}} \quad (6.7)$$

The contrast describes the ratio of the amplitude and the offset. The contrast is not to be confused with the fringe visibility $V$, sometimes referred to as contrast [159]. The contrast ranges from 0 to 1. A maximum contrast of 1 can be achieved for $R_f \sim 0.22$. For $R_f = 0.036$ and $R_{cl} = 0.345$ the contrast is $\approx 0.60$. By driving the cantilever and monitoring the contrast and fringe visibility, we obtain a relatively good optical alignment. However, at a certain distance from the fiber, we measure an offset of only 8.0% instead of 35.7%/2 = 17.8% for a cantilever at 0 $\mu$m distance. Obviously, angular mis-alignment and a limited numerical aperture can significantly reduce the returned reflected intensity. Thus, this dependency has to be considered.

### 6.2.3 The numerical aperture

The loss of intensity due to the restricted, outward angle of the light at the fiber-end (reflected via the cantilever) can be incorporated into Eq 6.5. Let us consider the losses from the projection of...
6.2. OPTICAL DESIGN

![Graph](image)

**Figure 6.11:** The normalized intensity $I$ as a function of the optical phase difference $\delta$.

the diverging light cone out of the fiber, reflected via the cantilever and projected back into the core of the fiber. Geometrical optics should be valid in this situation if the distances are bigger than the wavelength of the light (> 1 $\mu$m). In this case, the losses scale with the ratio of the two radii $a/(a + q)$, where $q$ is the projected radius $2x \cdot \tan(\alpha)$ and $a$ the fiber core radius. The reduced, reflected field $E_{2r}$ that couples back into the fiber is (see figure 6.12)

![Diagram](image)

**Figure 6.12:** Side view of the fiber-end and cantilever. $a$ is the radius of the core of the fiber, $q$ the projected radius and $\alpha$ the acceptance half-angle.

$$E_{2r}(x) = E_0 \cdot -r(1 - r^2) \cdot \frac{a}{a + 2x\tan(\alpha)}, \quad (6.8)$$

with $x$ the distance from fiber to cantilever. The numerical aperture is $\text{NA} = \sqrt{n_{\text{core}}^2 - n_{\text{clad}}^2}$ where $n_{\text{core}}$ and $n_{\text{clad}}$ are the refractive indices of core respectively cladding of the fiber. The NA of the Nufern HP 630 Fiber was 0.13, with $n_{\text{clad}} = 1.48$ and $n_{\text{core}} = 1.45$. The acceptance half-angle $\alpha$ in air, can be derived from $\alpha = \sin^{-1}(\text{NA}) \approx 7.4$ degrees. The corresponding intensity variation is plotted in figure 6.13a.

$$I(x) = A_0^2 \left( R_f + (1-R_f)^2 R_{cl} \cdot \left( \frac{a}{a + 2x\tan(\alpha)} \right)^2 + \frac{a}{a + 2x\tan(\alpha)} \cdot V \cdot \cos(\delta) \right) \quad (6.9)$$

Our interest is in the part that varies with the optical phase difference $\delta$. We want to maximize contrast and amplitude modulation. Therefore, we define an optical sensitivity $S$ which should have
the following distance dependency

\[ S \propto S_0 \cdot \frac{a}{a + 2x \tan(\alpha)}, \]

in which \( S_0 = A_0^2 \cdot V \). The distance dependency is measured and is in good agreement to this equation, see figure 6.13.

![Graph](image)

**Figure 6.13:** (a) Simulated normalized intensity I(x) as a function of the distance x. (b) Experimental sensitivity dependence on the separation distance between the cantilever and the fiber-end. The dotted line is the sensitivity in equation 6.10 with the fiber core radius \( a = 2.0 \mu m \) (close to the specified core radius of 2.15 \( \mu m \)), the half-angle \( \alpha = 7.4 \) degrees and \( S_0 = 100 \text{ MV/m} \). The dashed line data belongs to the right axis and displays the corresponding detection limit at 7 kHz (the eigen frequency of an empty cantilever). The distance x is estimated from the number of rotations and the pitch of the mechanical z-translation stage.

Furthermore, a linear distance dependency of the detection noise limit is measured. This is true if the detection limit is mainly caused by laser 1/f noise, which obeys \( \Delta x = x(\Delta \lambda/\lambda) \) [155]. A short summary can be made from the above calculations:

- **Numerical aperture.** With the current NA=0.13, most of the intensity of the light will not be coupled back into the fiber for more than 5 \( \mu m \) separation distance. Decreasing the NA, to for example 0.05, will increase the possible working distance to ~25 \( \mu m \). However, the angular accuracy of the optical alignment then becomes even more crucial. Furthermore, the setup will become more sensitive to dust particles.

- **Coating of the fiber-end.** A change in refractive index of the fiber-end will affect the fringe visibility, sensitivity and contrast. A maximum fringe visibility of 45% can be achieved for \( R_f = 0.33 \), for a coating with a relatively high refractive index of ~3.7, corresponding to a sensitivity enhancement of about 2 times. Additional sensitivity enhancement is expected due to the higher order reflections, especially when the two surface are close to perfectly parallel alignment.

- **Working distance.** A practical requirement is to have a noise floor below < 1 \( \text{pm}^2/\sqrt{Hz} \), which is needed for the optimal control to function properly. In MRFM design IIa at least 1 hour is
needed to optimize the $x, y, z, \phi, \theta$ position of the cantilever until this requirement is met. A typical working distance is 10 $\mu$m. A lower noise floor can be achieved for shorter distances, but there is a risk of the cantilever snapping to the fiber. In probe design I this would mean a complete start over. The Atto-cubes in design II make it possible to move the cantilever in the vacuum, risking this shorter working distance. A lens is used in design IIa for an increased fiber to cantilever working distance.

### 6.2.4 Using a lens in the interferometry setup

To increase the working distance of the interferometry setup, our first attempt is to insert a sapphire ball-lens with a diameter of 500 $\mu$m\[160\]. A ray-tracing simulation is done with a software package named "Solstis", the imaging distance is about 200 $\mu$m on both sides, thus the total distance from fiber end to cantilever then increases to $\sim$1 mm (see figure 6.14) and the Toshiba laser with a coherence length of 0.05 mm (see table 6.2) can not be used.

![image](figure_6.14.png)

**Figure 6.14:** Ray-tracing of a sapphire ball lens with the Solstis software package. Ball lenses are normally used in fiber-optic collimators and not for direct imaging since the focus spot is much wider. A better image can be obtained if two ball lenses are placed in series.

In practice, the ball lens is extremely hard to align to the fiber. The produced mechanics did not meet the required tolerances for the laser spot to be to properly aligned within the fiber core diameter of only 4 $\mu$m. In many factories, that produce such fiber optical components, the $x, y, z$ lens alignment is automated with $\mu$m precision, after alignment the lens is fixed to the fiber.

**Brimrose lens**

Since the mechanical alignment of the ball lens is very demanding, we decide to use a lens, which is already attached to a fiber (see figure 6.15)[161]. The lens is an aspheric Grated Reflected Index (GRIN) lens with a focus distance of 2 mm. To use a lens with this working distance, a laser with a longer coherence length is needed, the ATFM 102. The fiber with integrated lens from the company 'Brimrose' is originally intended for collimated, fiber-optic illumination and not for 1:1 imaging. Inside, the fiber-end is coated to reduce the amount of back-reflected light. However, after conversation, the integrated lens and fiber-end are modified to our needs by Brimrose to return transmitted back-reflections into the fiber with a higher efficiency. Furthermore, for this special, the spot size radius is specified to decrease from 50 to 10 $\mu$m. The NA of this fiber was 0.11, this is the limiting aperture angle of the optical circuit.
In the bare fiber setup, the reflected power increases linearly with the forward power. By aligning the laser spot off the cantilever (with or without lens) and by dividing power levels we obtained a maximum experimental value of $R_{f}^{\text{max,exp}} = 4\%$. This value could be reproduced quite accurately and can be used to check if the fiber is in good shape. Interestingly, the Brimrose lens reflected power showed non-linear behavior (see figure 6.16).

![Figure 6.15: Images of the Brimrose lens (right) attached to a ‘fiber with FC/APC connector’ (left).](image)

**Figure 6.15:** Images of the Brimrose lens (right) attached to a ‘fiber with FC/APC connector’ (left).

![Graph](image)

**Figure 6.16:** The forward and reflected power relation with and without Brimrose lens. There was no cantilever at the fiber-end.

The ratio between forward and reflected power can be obtained from the slope of the graph. This ratio is lower than without the lens, which can indicate angular mis-alignment. A mis-alignment will decrease the reflected power ratio. The non-linear behavior is more difficult to understand. It is not caused by saturation of the photo-diodes and the Thorlabs photo-diode response is approximately linear in the selected range. A possible explanation can be heat absorption from the laser resulting in a $\mu$m deformation or displacement of the lens.

A cantilever is placed at the end of the fiber and the contrast and fringe visibility are monitored. Because of the strong distance dependency of the contrast and visibility, a quantitative comparison between the setups is difficult. The non-linear behavior is observed again in the fringe visibility with Brimrose lens (see figure 6.17). Note that the fringe visibility was maximal 3% in this measurement. If we used the lens at forward power levels above 50 $\mu$W, the contrast dropped. At these high powers
a deviation from the normal sinus shape was visible while moving through the fringes. Due to the different path lengths caused by the aberrations in the lens, there is an irregular interference pattern. The same dependency is observed when the spot is focused on the area of the larger cantilever chip. The Brimrose lens is not intended for imaging, but for collimation of a laser beam. With a long working distance and a 4 µm core, the specifications of the wavefront are demanding and optical aberrations at the outer edges of the lens deform the wavefront.

The Brimrose lens in combination with ATFM 102 laser functions properly and we are able to obtain the cantilever spectrum with a sufficiently low background noise. However, the alignment procedure is too time consuming. An iterative approach is used to obtain maximum sensitivity. Because of the extremely tight angular requirement, the alignment process takes a minimum of three hours, up to more than a day and has to be repeated for each new cantilever. Optimal optical alignment, with \( R/F \geq 4\% \), is required to have a low detection noise floor. Every cantilever is glued under a slightly different angle onto its mount and the angular tolerance with Brimrose lens is only approximately \( \text{atn}(0.002 \text{mm}/10 \text{mm}) = \pm 0.01^\circ \). The angular tolerance of the bare fiber is much more acceptable \( \text{atn}(0.002 \text{ mm } / 0.020 \text{ mm}) = \pm 5.7^\circ \). The setup with Brimrose lens is sensitive to the bending of the cantilever. Even for an empty cantilever, the position of the spot on the cantilever yields different sensitivities.

### 6.2.5 Practical optical design issues

Several practical aspects of the optical circuit should be considered with care.

**Connectors.** Back-reflections will be minimal when using FC/APC connectors. These have a 8 degree tilted angle with respect to the light propagation direction. A FC-PC connector is not useful, since it picks up all vibrations at the connector interface. An older standard for fiber optical cables makes use of ST connectors.

**Fiber.** The polarization changes from transitions or from bends in a single mode fiber cause phase errors in the output signal. The size of this error depends on the reflectivity of the cantilever.
and fiber, the number of bends and the shape of the light pattern inside the fiber. A mono-
mode polarization-maintaining fiber can minimize this error, but this is not needed in the
current setup because slow (temperature) changes can be compensated with the piezo feedback
at the fiber-end. The fiber has a low attenuation per meter at the wavelength of the laser.

**Coupler.** The 50/50 2x2 Gould Fiber optic bi-directional coupler functions as a free space beam-
splitter. The difference with a beam splitter is that in general couplers are more wavelength-
dependent. Couplers are more sensitive to temperature or vibration effects; therefore they are
not well suited for polarization applications. For a free space beam-splitter, the transitions
from fiber to air to glass and to air cause undesired back-reflections, which causes a decrease
in contrast. If this surface is vibrating only slightly it picks up ‘noise’ in the interferometer
application.

**Photo diodes.** For high (single photon) sensitivity avalanche photodiodes can be used. Their
dynamic range is smaller, but they have a higher signal to noise ratio. They require high
voltage operation > 100 Volt and a very stable power source. The sensitivity of two normal
Silicon Thorlabs PDA 36A-EC photo-diodes was sufficient, but the highest amplification factor
of 70 dB is needed in the reflected signal branch.

**Fiber surface and reflectivity.** The reflectivity of the cantilever and output fiber has to be con-
sidered carefully. The maximum fringe visibility is ~0.2, but the visibility is strongly depen-
dent on the distance (see equation 6.9). The fiber-end can easily become dirty with small
dust particles. Therefore, it is important to inspect the fiber-end periodically with an optical
microscope.

**Drift feedback.** Thermal tuning of the wavelength is an option to keep the working condition
around the center of the fringe [156]. A disadvantage can be the relatively slow thermal response
time. In design I the feedback was provided mechanically by the fiber piezo, in design II by
the z-piezo of the Atto-cubes.

**Laser.** The laser requires extra attention for stable operation in many aspects which will be dis-
cussed here.

- Temperature control. The most common way of Thermo-Electric (TE) feedback is with a
  Peltier element.

- Isolator. An isolator is used to prevent laser light going back into the laser, which causes
  heating and interference effects. It is important to place the first optical element far (>0.5 m)
  away from the laser to reduce the strength of stray reflections from surfaces.

- Circulator. An internal circulator is used to create a proper circular beam shape (laser beam
diameter of 5 mm for the ATFM 102).

- Mode hopping. A certain optical output mode of the laser exists within a certain temperature
  range. When the temperature is not regulated or disturbed due to optical feedback, the laser
  diode will mode-hop and the different modes will be coupled into the fiber. Each mode having
  its own frequency and phase.

- Wavelength. When the wavelength changes slightly, the interference pattern can change.
  Wavelength drifting, slower than 0.1 nm/s is compensated with the fiber-piezo feedback loop.
• Coherence length. \( \ell_c = \lambda^2 / (\Delta \lambda) \), in air \((n=1)\) with \(\Delta \lambda\) the laser wavelength bandwidth. The coherence length of a normal laser diode in general is normally quite short \((\pm < 0.1 \text{ mm})\). A Distributed Feedback (DFB) laser diode, a Vertical Cavity Surface Emitting Laser (VCSEL), a Helium-Neon laser or a quantum well laser diode can be used for longer coherence lengths. However, the interference from the fiber end reflection and the cantilever reflection has to occur within the coherence length of the laser. The coherence length cannot be too short. The difference between the four fiber lengths at each side of the bi-directional coupler should be larger than the coherence length or the fiber ends need to be polished under an angle to avoid stray reflections of these fiber ends. A laser with a too long coherence length is therefore also not preferred. Lasers with a long coherence length are more sensitive to stray reflections back into the laser. The back reflections can cause mode hopping and laser instabilities.

• Polarization. A laser diode is usually linearly polarized. Since the light is linearly polarized, a polarizer can be used to attenuate the light.

### 6.2.6 Laser noise

It is important to have low laser noise, since the detector noise floor is dominated by \(1/f\) laser noise at low frequencies. Next to the specifications of the laser, the voltage noise spectra of four different lasers are recorded to determine the most suitable laser. Laser noise originates from different factors. Here we describe the three most important factors. First, laser intensity or amplitude noise can be measured directly with a photodiode and it is specified in table 6.2 by a root-mean-square value, representing the square root of the integral of the power spectral density over a frequency range. This type of noise can be canceled for by subtracting the forward laser power. Second, there can be timing jitter noise of the laser. This type of noise is more applicable to a mode-locked laser and we do not consider it here. Finally, the most important type of noise is frequency noise of a laser, which is directly related to laser phase noise. This laser phase noise is translated to amplitude noise by the interferometer optical setup. This amplitude noise on the photo-diode detectors can not completely be averaged out since it adds differently for each of the two photo diodes with the already present amplitude noise from the laser in each branch. The origin of this laser phase noise is quantum noise from the spontaneous emission of the laser, which causes the laser’s finite line width. In principle, this type of noise can be quantified with a noise power spectral density. Here, the amplitude voltage noise spectra are compared. In table 6.2 some specifications of the lasers are shown. The Toshiba laser diode is a TOLD 9215, it has an integrated Feltier temperature controller, a wavelength of 673 nm and a line width of 10 nm (coherence length of 4.5 mm). Its maximum laser output power is 5 mW. The Gaussian laser beam output profile is calibrated. The Photonic laser module is TE-cooled. The Coherent ULN series uses 80 MHz modulation over its mode regions. The Analog Technologies ATMF 102 is a TE-cooled laser with ellipsoid beam profile. It has a build in circularizer, for the beam shape and a narrow line width of \(< 17 \text{ MHz} \), \( \sim 0.1 \text{ nm} \), while the other lasers had a line width \(> 1 \text{ nm} \). The laser output was directly coupled into the fiber and monitored with the photo-diode, which was coupled to the PC. The settings of the measurement are described here.[162]

By applying a 1k\(\Omega\) load to the ADC input of the PC, it is observed that, the noise floor of the ADC of the PC for \(\pm 1\text{V}\) dynamical range is sufficient, i.e. \(\sim 0.3\mu\text{V}/\sqrt{\text{Hz}}\), see figure 6.19. A
Table 6.2: Important specifications of the four lasers.

<table>
<thead>
<tr>
<th>Laser</th>
<th>( \lambda ) (nm)</th>
<th>( \Delta \lambda ) (nm)</th>
<th>Coh. length (mm)</th>
<th>Ampl. noise (%V\textsubscript{rms})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toshiba TOLD 9215</td>
<td>673</td>
<td>&lt;10</td>
<td>0.05</td>
<td>&lt; 1 (DC-5MHz)</td>
</tr>
<tr>
<td>Photonic TEC 300-0601-00</td>
<td>635</td>
<td>&lt;10</td>
<td>0.05</td>
<td>&lt; 0.06 (10Hz-10MHz)</td>
</tr>
<tr>
<td>Coherent ULN series</td>
<td>635</td>
<td>&lt;5</td>
<td>0.08</td>
<td>&lt; 0.01 (10Hz-2MHz)</td>
</tr>
<tr>
<td>Analog ATMF 102</td>
<td>665</td>
<td>&lt;0.1</td>
<td>4.4</td>
<td></td>
</tr>
</tbody>
</table>

Figure 6.18: The real, voltage noise spectra of different lasers at a laser output power of \( \sim 20 \mu W \).

Dynamical range setting of \( \pm 10 \text{ Volt} \) increased the detector noise floor of the ADC of the PC to \( \sim 3 \mu \text{V/\sqrt{Hz}} \). The photodiode thermal noise floor, recorded with no laser power, is below this noise floor. The resonances at 50/100/200 Hz are eliminated, when the power supply Delta E15-02 of the subtraction electronics is replaced with a battery source. The phase of the noise, induced by the power supply, is different from the phase of the laser, however, their contributions to the real voltage noise spectra add up. From figure 6.18 it is observed that the Toshiba and the Coherent laser noise have a 1/f noise characteristics, while the Analog laser noise has a near linear dependency on the frequency. The Photonic TEC laser module suffers from strongly increased noise near 3 kHz, the laser seems strongly disturbed by the reflected stray light. Diode laser frequency noise is dependent on the current and the temperature. In all the four lasers, the temperature is kept constant with electronic feedback. The Toshiba, the Coherent and the Photonic laser have the largest laser line widths and the strongest 1/f dependence. The Coherent laser seems to have the lowest voltage noise, a slightly lower 1/f noise than the Toshiba, but it has a strong, unwanted resonance near 900 and 2000 Hz. The ATMF laser has the lowest frequency/amplitude 1/f noise. The Analog Technologies ATMF 102 is designed for low amplitude noise and narrow laser wavelength. However, due to the increased coherence length, the noise that is picked up along the optical circuit increased. The ATMF 102 is most sensitive to stray reflections. The use of a short coherence length diode laser improves low-frequency stability by eliminating interference effects of stray reflections [155]. In
many CD players for example, the coherent laser signal is down modulated to an optimal coherence length to reduce the lasers vulnerability to stray reflections. The ATMF 102 is tested because of the need for a longer coherence length, in case a lens is inserted between the cantilever and fiber. However, it is difficult to obtain a constant 'base line' noise level with this laser, even with a -40 dB isolator. The ATMF start up time, to reach a constant temperature, is about 30 minutes. After this time, the sensitivity to air flow, temperature and reflections still causes fluctuations. To conclude, the Toshiba TOLD 9215 laser diode is most suitable. The noise spectrum does not contain any peaks in the relevant frequency range (100-7000 Hz). With the Toshiba laser and 1/f amplitude noise reduction, it is possible to reach detection limits below 0.1 pm²/Hz. The ATMF 102 needs to be used in combination with the isolator and is only applied when a longer coherence length is necessary.

6.2.7 Instrumental aspects of the fiber-optic interferometer

The final, most workable fiber-optic interferometer design is described in figure 6.7. The linearly polarized Toshiba diode laser beam passes through a 40 dB optical isolator (Thorlabs IO-3D-670-VLP), with an aperture of 3 mm, to reduce laser noise and to prevent mode hopping. If needed, a polarizer can be placed in front to reduce the output power. A 20x microscope lens with a NA of 0.17 and a Thorlabs x, y, z fiber alignment stage MBT612/M is used to couple the laser light into a Gould Nufern 630HP fiber-optic 2x2 bi-directional 50/50 coupler. The fiber has a Numerical Aperture (NA) of 0.14. The fiber is mono-mode and has an outer jacket of 900 μm, a cladding diameter of 125 μm and a core diameter of 4.3 μm. In the branch toward the probe an angle polished fiber connector (FC/APC) is placed to allow easy (dis-)connection of the probe. Two 400-1100 nm switchable gain 0-70dB Silicon detectors from Thorlabs PDA 36A-EC are connected to the forward and reference branch of the coupler. A typical gain for the forward photo diode is 50 dB and the reflected photo
diode 70 dB. The laser amplitude noise in the reflected signal branch is subtracted as described in figure 6.5. When a triangular voltage swing is placed on the fiber piezo, the interferometry signal shows a sinus function. When this sinus crosses its zero level, the slope and sensitivity are maximal. The displacement sensitivity is then almost linear, since \( \sin(x) = x \) for \( x \ll 1 \). The forward laser power is set to the optimal forward laser power \( \sim 50 \mu W \) (see Eq. 5.20). Peak displacements of \( \sim 50 \) nm can occur when the RF power is switched on. A drift feedback is implemented to compensate long term temperature drifting. The standard deviation of the vibration of the cantilever, with optimal control enabled, is less than 0.2 nm.

6.3 Strip line design

The basic radio frequent resonant circuit in an NMR of MRFM setup is a coil. A different type of RF-element is a so called 'strip line'. A strip line circuit is a strip of metal on top of a substrate of insulating material, normally confined by two parallel ground planes[163] for homogeneity reasons. In MRFM, \( B_0 \) homogeneity is not really an issue, instead mostly the generation of a strong transversal magnetic \( B_1 \) field strength in the strip line is very advantageous, since this can invert more spins in a broader slice during the FAPs. This will give a higher SNR. Furthermore, the application of strong RF pulses can be useful to affect more spins in a broader slice. Technically, other advantageous of the strip line are the scalability to smaller dimensions, the ability for precise alignment, very close (\( \mu m \)) to the sample and the possible (system) integration on chip. The strip line can be processed lithographically. Novel strip lines are fabricated in the MESA+ clean room, with the aid of J. Bart from the University of Twente. In the following section the strip line fabrication process and performance is described.

6.3.1 MRFM strip line design

Different strip line designs are created on a single wafer. The 'slit design' has two parallel strips, see figure 6.20 and the 'hole design' has a circular aperture in the center of the strip-line, see left photo in figure 6.21. The 54 strip lines on the wafer have different sizes. The slit or hole size is 10/20/30/40 \( \mu m \), the width of the copper is 10/20/30/40 \( \mu m \) and the length can be 50/100/120 \( \mu m \). The right photo of figure 6.21 shows an overlay of the four masks of one strip. One of the designs does not have a hole for the optics. In this design, it is opted to use the last upper part of the Silicon thin film as part of a Fabry Perot cavity for the laser interferometry. However, the bottom surface is etched with Reactive Ion Etching. The bottom is therefore relatively rough on a sub \( \mu m \) scale and the laser light can not propagate sufficiently strong through the 100 \( \mu m \) silicon layer. The designed strip lines should be handled with care. Due to the well defined crystal plane, it is relatively easy to cleave or break along a crack in the wafer. The small laser hole has such an effect. A weak pressure applied from the top will cleave the silicon carrier along its cleaving plane. The strip lines are carefully mounted in the MRFM setup with small teflon rings.
Figure 6.20: Slit design (left) Bottom view, showing the hole for the gradient with a diameter of 320 µm. A part of the RF strip line is visible. (right) Top view. Slit spacing is 30 µm, the width of one strip is 30 µm, the length is 120 µm. The hole in the center allows transmission of the laser beam.

Figure 6.21: (left) Top view of the hole design. (right) Overlay of the four designed masks, of one of the 54 strip lines on a wafer. The circle in the center has a diameter of 320 µm.

6.3.2 MRFM strip line processing

The processing of the wafers is divided here into four sections A, B, C, D. This is done on the basis of the four different masks which are needed in the different lithography processes.
<table>
<thead>
<tr>
<th>A1. Silicon wafer, cleaning and marking</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2. Thermal growth of 2 μm SiO₂ on both sides</td>
</tr>
<tr>
<td>A3. Front side etched with protective foil on the rear</td>
</tr>
<tr>
<td>A4. Lithography to create the gradient hole</td>
</tr>
<tr>
<td>A5. Pattern SiO₂</td>
</tr>
<tr>
<td>B1. Deposit seed layers 8 nm Ti + 50 nm Cu</td>
</tr>
<tr>
<td>B2. Lithography copper, pos. resist, 25 μm AZ9260</td>
</tr>
<tr>
<td>B3. Deposit copper structure 17 μm height</td>
</tr>
<tr>
<td>B4. Resist removal</td>
</tr>
</tbody>
</table>

Table 6.3: Processing step A: the gradient holes were patterned from the rear side of the wafer with a buried mask. Processing step B: the front side copper mask

### 6.3.3 MRFM strip line performance

The strip line was designed to be of maximum RF field strength, while the RF homogeneity was compromised. The spins in a 'homogeneous' volume respond similarly to the applied RF field. This can be important for pulse excitation and might be useful during MRFM detection, but more important for MRFM is to have a high RF field strength. This is because the strength of the RF field determines if the spins remain locked during the adiabatic sweeping. Furthermore, in case of high spatial resolution in MRFM, strong gradient magnetic fields are needed and the frequency sweep range increases, leading to the need for stronger $B_1$ fields.

A single copper strip line of 40 μm width and 17 μm height could easily withstand 25 Watt for more than 10 seconds without visible damage. The strip line would only heat up less than 1 degree, because of the favorable silicon heat conductivity and the large copper heat sinks. Because of the integrated design, the copper is placed directly on the support and no additional substrate layer is needed. Furthermore, the gradient can also be positioned in the support. The MRFM strip line was
Table 6.4: Processing step C: the laser and gradient hole were etched from rear side. Processing step D: the powder blasting of the holes for the mounting of the chip.

placed in a special probe, with a resonating electronic circuit at 600 MHz. The probe was tuned and matched with a $Q \sim 50$, $B_1 \propto \sqrt{Q}$. A side view of the stripline in MRFM design II is given in figure 6.22.

Figure 6.22: Side view of the dimensions of the sample and the double slit strip line (not to scale). The length of the strip line was 120 $\mu$m.

Note that in MRFM design I, the sample has to be placed outside the center of the coil and as a consequence the $B_1$ field is significantly reduced ($\sim 50\%$). Strip line excitation has been employed
earlier in MRFM,[123] reducing the required RF power level and offering the possibility to place the sample in the center of the field flux lines.

\(^1\)H echo-nutation data on silicone rubber was acquired to verify the RF field strength and profile, see figure 6.23. The NMR nutation data was obtained from a sample with an estimated volume of 0.007 mm\(^3\). The average RF field was 130 kHz at a power of only 1.0 Watt. Due to strong RF inhomogeneity of the field, a distribution in the RF field was observed in the nutation spectrum. The \(~130\) kHz RF field implies a linear \(B_1H\) field with an amplitude of \(~3.1\) mT. The RMS \(B_1\) field is 2.2 mT. Knowing the \(B_1\) field, the average resonant sample height can be estimated using the closed loop integral form of Ampère’s law

\[
\int B \cdot ds = \mu_0 I
\]

(6.11)

where \(I\) is the current. Substituting the current and the average \(B_1\) obtained from the nutation in this equation, at this power, the average resonant sample height \(\Delta z\) is 13 \(\mu m\).

![Figure 6.23](image)

**Figure 6.23:** (left) \(^1\)H spectrum at different nutation times. The FWHM of the spectrum of silicone rubber was 1.6 kHz. (right) Fourier transform of the nutation, showing the RF field profile. A zero point is added at the beginning of the series. 90 degree zero-th order phasing was applied.

In figure 6.24 the \(B_1\) field of the strip line is compared to that of a micro-coil at the same power with a 50 ohm load. The two systems are compared by considering field strengths at equal currents. At equal currents, the 5 turn micro-coil has a higher RF field.

Different conclusions can be drawn when we compare the two systems at equal heating of the resonator. The 50 \(\mu m\) copper wire of the micro coil has a cross-sectional area where the current runs through of \(\pi \cdot R^2 = 1960 \mu m^2\), while the double slit copper strip line has a lower cross-sectional area of 1360 \(\mu m^2\) and thus a slightly stronger current density. The resistance and heating however are proportional to the volume of the resonator. The strip line length is much shorter, \(i.e.\) 120 \(\mu m\) than the coil wire length of 3900 \(\mu m\) (5 coil turns). The ratio of the resonant copper volume is therefore significant (coil / stripline) \(~47\). Which means that, at identical heating of the resonator, the current is 47 times lower and the generated RF field is scaled accordingly.

Generally speaking, at identical heating the strip line outperforms the micro coil at close distances. The strip line offers more advantages in comparison with the micro coil:

1. The mechanical stability is better. The sample can be accurately positioned in the center and is optically accessible from one side.
Figure 6.24: The strip line and micro-coil $B_1$ field strength as a function of the distance separation in $z$-direction. The applied power is $P = 1$ Watt, $R_{\text{load}} = 50\Omega$, $B_{\text{strip}}(z) = \mu_0 \cdot I/(2w + 2h + 4z)$, with $w$ and $h$ the width and height, $B_{\text{coil}}(z) = \mu_0 \cdot I \cdot N \cdot R^2_{\text{coil}}/(2 \cdot (R^2_{\text{coil}} + z^2)^{3/2})$, with $R_{\text{coil}} = 125\mu\text{m}$, $N = 5$ windings.

2. The required RF power for (and heating of) the strip line is lower since its resistance is lower. Furthermore, the heat can be more easily distributed in the strip line, since it is placed on a (for example silicon) carrier. Silicon has a good heat capacity and is an excellent conductor for thermal flow.

3. The cross-sectional area can easily be made smaller than 50 $\mu\text{m}$ using lithography. The ratio $B_1/I$ can then further be enhanced, aiming for a very strong, local RF field.

In conclusion, the strip line is a preferable choice for MRFM of small samples at short working distances, where stability and RF field strength are key issues. To achieve these higher RF fields, the RF homogeneity is compromised.
Chapter 7

Magnetic Resonance Force Microscopy - Measurements

In this chapter we will show different MRFM measurements. We discuss the experimental procedure, the gradient strength dependency, the reproducibility and we show experimental MRFM data of an AlGaAs image and discuss the SNR that would be needed to image a thin film with 100 nm spatial resolution.

7.1 Practical MRFM example I

A convenient sample for MRFM with favorable conditions, $T_{1p}$ and $T_1 \sim 5$ seconds is Ammonium-sulfate (NH$_4$)$_2$SO$_4$. First, the sample is put on the cantilever as described in Appendix C. Amorphous Silicon Nitride cantilevers are commercially available. They have a relatively low spring constant of $k_c = 0.01$ N/m and an unloaded resonance frequency near 7 kHz. In practice, the quality factor of the cantilever in vacuum, $\sim 10^{-6}$ mbar, ranged from 500 - 15,000. The cantilevers should not be coated with metal, since this can causes a bimorph effect when the cantilever is heated by RF waves[3].

7.1.1 Sample mass

The mass of a sample is derived from the cantilever resonance frequency. Simultaneously, the mass can be approximated using the density of mass of the sample and its outer dimensions. We determined the resonance frequency with MRFM design I, see Section 6.1. The cantilever resonance frequency was $f_c = 1225 \pm 10$ Hz and the spring constant was $k_c = 0.01 \pm 0.001$ N/m, thus the mass of the sample can be calculated $k_c/\omega_c^2 = 169 \pm 17$ ng.

The optical microscope was equipped with a grid to measure micrometer distances. The optically determined outer dimensions of the volume of the crystal gives an over-estimation of the real volume. The optically measured outer dimensions are $V_{outer} \sim L \times W \times H \approx (90 \pm 10 \times 60 \pm 10 \times 25 \pm 10) \mu$m.

155
Figure 7.1: Image of the cantilever chip and micro coil (MRFM design I). The longest cantilever has a length of 320 μm. The ammonium-sulfate sample was glued on top. The copper wire of the coil is coated with isolation. The wire has an outer diameter of ~50 μm.

Figure 7.2: Resonance spectrum of the loaded cantilever under vacuum without optimal control feedback. The noisy solid line represents the open loop cantilever spectrum. The theoretical solid line through this data is Y(ω) in Equation 7.1, with Q_{open} = 1007. The Q factor of this particular cantilever was poor. The lowest solid line displays the laser 1/f noise.

The density of mass ρ = 1769 kg/m³. This gives an over-estimated mass of 239±106 ng. Assuming equal roughness across the volume of the sample, a correction factor can be applied to obtained the lower, effective volume. The mass derived from the cantilever frequency is assumed to be most accurate. The effective volume is V_{eff} = 0.70 \cdot V_{outer} \approx (63 \times 42 \times 18) \mu m.
7.1. Practical MRFM Example I

![Diagram of MRFM detection pulse sequence]

**Figure 7.3:** The commonly used MRFM detection pulse sequence. $A$ labels the amplitude of the RF waves and $f$ the frequency. The insweep and the sweep half-amplitude are frequency offsets.

### 7.1.2 The cantilever spectrum

The micro coil was accurately aligned on the cantilever holder, as is displayed in figure 7.1. The cantilever with coil and sample is placed in the MRFM probe and then inside the magnet. We follow the calibration procedure described in Appendix I. The cantilever resonance spectrum is shown in figure 7.2. The amplitude of the $1/f$ laser-noise spectrum is $A/\omega$, the detector thermal noise floor $B$ and the fitted graph is $Y(\omega)$

$$Y(\omega) = \frac{S_u}{(1 - \omega^2/\omega_0^2)^2Q^2 + \omega^2/\omega_0^2} + A/\omega + B,$$  \hspace{1cm} (7.1)

where $S_u$ represents the movement of the cantilever tip due to Brownian motion [164] The cantilever damping constant was $\Gamma = 1.3 \, \text{mg/s}$.

### 7.1.3 Spin temperature cycling

In MRFM experiments the cantilever can be excited unintentionally at the eigen-frequency by the irradiation of the RF waves. This is called cantilever heating. It is therefore needed to distinguish between the cantilever heating and the spin signal. It is possible to diminish the cantilever heating using special RF sequences during detection. Such sequences, for example amplitude ramping of a sawtooth with a periodic $180^\circ$ phase-shift, allow the acquisition of the MRFM spin signal in a single scan. This sequence was first proposed by Degen, et al. [65]. Another alternative to remove the cantilever heating contribution is via spin temperature cycling. In spin temperature cycling two scans are needed. In one scan a pre-sweep is done before the detection, inverting the magnetization, while in the second no pre-sweep occurs. Via subtraction of the two scans, the spin signal adds, while the cantilever heating cancels out since it had the same phase. It is also possible to apply spin temperature cycling only during detection. In the first scan, the FAP sweeping starts from above resonance, in the next acquisition the FAP sweeping starts from below resonance, see figure 7.3. The heat noise cancelation is visible in figure 7.4a. The smooth overlaying positive/negative curves represent the integrated MRFM signal from two scans, containing the heat noise and the spin signal. Since the $Q$ of the probe is $\sim 1$, the heat noise was determined by the power output, which was determined by the high-power band-pass filter. If the frequency response of the RF circuit is not flat, the cantilever can pick up more heating/power, depending on the frequency. Spin temperature
cycling can reduce this effect. However, the cancelation of the cantilever heating will not function properly if the heating contribution changes over time. This effect was observed at higher RF powers (> 3 Watt) for interleaved scanning (see Section 8.1).

**Gradient** A ferro-magnetic cylindric rod generates a gradient magnetic field. The magnetic field distribution depends on the shape of the gradient source. The magnetic field distribution can be simulated numerically using finite elements. Different gradient shapes were discussed for MRFM [3, 65]. From the Maxwell Equations we derive the magnetic flux density for a cylindrical rod along the z axis. The saturated magnetic field of the iron gradient $B_{sat} = 1.9 \text{ Tesla}$ and $M_{sat} = B_{sat}/\mu_0$. The rod has a length of $L \approx 13 \text{ mm}$ and the radius $R = 150 \mu\text{m}$, so that $L >> R$. The magnetic field as function of the $z$ position is

$$H_M(z) = \frac{M_{sat}}{2} \left( \frac{z + L}{\sqrt{R^2 + (z + L)^2}} - \frac{z}{\sqrt{R^2 + z^2}} \right) \approx \frac{M_{sat}}{2} \left( 1 - \frac{z}{\sqrt{R^2 + z^2}} \right) \quad (7.2)$$

$$B(z) = \mu_0 (H_0 + H_M(z)) \quad , \quad (7.3)$$

with $H_0 = B_0/\mu_0$, $B_0 = 4.23 \text{ Tesla}$ (180-180 MHz). The resonance frequency can be found using

$$\nu_0 = \frac{\omega_0}{2\pi} = \frac{\gamma B(z_0)}{2\pi} \quad , \quad (7.4)$$

in which $z_0$, the distance from the gradient to the center of mass position of the sample, can now be calculated from the resonance frequency. The central resonance frequency was 185.4 MHz, which
corresponds to 4.36 Tesla and \( z_0 = 345 \mu m \), at this distance \( \partial B/\partial z(z_0) \approx 600 \) T/m. The resolution is 26 kHz/\( \mu m \).

**Number of spins** The number of spins can be calculated using Equation 1.10. Using the experimentally determined gradient strength and force detection limit of only 2.2 fN for this relatively low \( Q \sim 1000 \) cantilever, the minimum amount of detectable \(^1H\) spin in a single scan with a SNR of 1 corresponds to \( F_{\text{min}} \approx 1.5 \cdot 10^{13} \) \(^1H\) spins. We can estimate the total number of \(^1H\) spins from the mass and the spin density. The total number of \(^1H\) spins is \( \sim 6 \cdot 10^{15} \). The effective full slice amplitude is 0.8240 = 192 kHz, corresponding to an effective slice height of 7.3 \( \mu m \). From the MRFM image it is determined that slice 19 contains approximately 55% of the signal. The maximum fitted \( T_{1}\rho \) was 2.6 seconds.

**SNR** The theoretically predicted single scan SNR from this slice is 138 (see Eq. 5.27). The corresponding theoretically expected force from the spins in this slice is 316 fN. The experimental, integrated force was 109 fN (see Eq. 5.39). However, the acquisition time was too short, \( i.e. \) 3 second. The generated RF field was 40 kHz at a power of 3 Watt. The sweep time for one period of the sawtooth was 0.816 ms and the adiabaticity was sufficient \( A \sim 22 \).
7.2 Practical MRFM example II - Gradient strength

A different sample of (NH₄)₂SO₄ was placed on a different cantilever. Due to the higher $Q$ factor, the detection limit and the friction coefficient were lower, i.e. $1.3 \text{ fN/}\sqrt{\text{Hz}}$ respectively $\Gamma = 0.11 \mu\text{g/s}$. The estimated and back calculated sample dimensions are $L \times W \times H \approx (43 \times 53 \times 31) \mu\text{m}$.

Figure 7.5 shows the MRFM images at different gradient fields. Increasing the gradient strength (and spatial resolution) reduces the SNR, since less spins are detected in a slice when the sweep amplitude remains similar. The expected total number of spins in this sample, based on the mass is $4.5 \cdot 10^{15}$. The sum of all integrated, corrected data points was approximately similar, i.e. 4.2, 3.8, $4.7 \cdot 10^{15}$ spins. At a higher gradient field, the image extends over a wider frequency range. If a bandwidth filter is used, the amplitude and phase should remain constant over the entire MRFM scan range. Furthermore, the applied RF power and the frequency dependence of the rest of the RF circuit should not vary much as a function of the frequency. The highest achieved gradient field strength with design I was 2500 T/m, at which point the gradient started to become too close to the sample and there was too much electro-static surface noise.
Figure 7.5: (a) 3D surface plot of the MRFM measurement at 530 T/m. (b) Contour plot of the $^1$H MRFM signal of ammonium sulfate at three different gradient strengths from 2 averages. The pulse delay was 15 seconds. The acquisition time was 1 second. The sweep half-amplitude was 150 kHz and the insweep frequency was 200 kHz. The preheating time was 1 second. The lock-in time constant was 100 milliseconds, $Q_{open} = 12.300, 14.700, 11.800, Q_{closed} = 20$. The gradient strength increased from 530 to 970 to 1940 T/m, corresponding to the $^1$H center frequencies of 184.2, 186.4 and 190.7 MHz. The frequency step size of the scans is 200, 400, 500 kHz. (c) $^1$H 1D integrated image of ammonium sulfate at different gradient strengths of 2 averages. $S = 17.4, 16.6, 19.3$ MV/m. $T_{1p}^{max} = 0.96, 0.90, 1.83$ s. A correction factor was implemented for under/over sampling within the $z$-grid of the image. This was done by multiplication with the varying frequency step size divided by the constant detection bandwidth of 400 kHz ($x_0.5, x_1, x_1.25$). The vertical scale displays the corrected number of spins, which was calculated on the basis of Eq. 5.39 and Eq. 1.10. The distance from the gradient was calculated with Eq. 7.2.
7.3 Practical MRFM example III - Reproducibility

The reproducibility of MRFM probe design I was tested on the same sample. The results from a series of tests are displayed in figure 7.6, their parameters and settings in table 7.1.

**Figure 7.6:** (a) Contour plot of the raw MRFM voltage signals with identical, absolute contour levels. Test 1 to 4 are displayed from top to bottom. The test configurations are displayed in table 7.1. (b) The integrated time signals, signal intensity loss due to loss of RF power, see text. (c) The integrated time signals converted to a force, as function of $S, k_c, Q, T_{1p}$, according to equation 5.39. The experiments were not interleaved, but sequential.

The reproducibility in the MRFM integrated amplitude was reasonable, although, in general, a loss of signal intensity was observed over time. The 40% absolute signal loss over time is attributed to loss of RF power. A drift in position of the micro coil over time could lead to a weaker RF field. The micro coil was not directly fixed to it's support and the long 50 µm wire, see figure 7.1, could deform by temperature variation. A decrease of the $T_{1p}$ over time was also noticed. The pulse
<table>
<thead>
<tr>
<th>Test number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting time</td>
<td>1:52 PM</td>
<td>2:23 PM</td>
<td>5:40 PM</td>
<td>6:12 PM</td>
</tr>
<tr>
<td>No. of averages</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>Sweeptime (ms)</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Pretime (s)</td>
<td>0.5</td>
<td>0.25</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Q&lt;sub&gt;open&lt;/sub&gt;</td>
<td>9700</td>
<td>10200</td>
<td>9000</td>
<td>9000</td>
</tr>
<tr>
<td>S (MV/m)</td>
<td>19.2</td>
<td>18.0</td>
<td>18.8</td>
<td>18.8</td>
</tr>
<tr>
<td>Max. T&lt;sub&gt;1ρ&lt;/sub&gt; (s)</td>
<td>1.1</td>
<td>1.2</td>
<td>1.2</td>
<td>1.0</td>
</tr>
<tr>
<td>Max. SNR&lt;sub&gt;time&lt;/sub&gt;</td>
<td>4.3</td>
<td>4.1</td>
<td>3.9</td>
<td>4.1</td>
</tr>
</tbody>
</table>

**Table 7.1:** A series of measurements took place within a total time span of 7 hours. The desired Q<sub>close</sub> was set to 20, f<sub>c</sub> = 1436 Hz, m = 122 ng, τ<sub>L</sub> = 0.1 s. The integrated MRFM signal, the half sweep amplitude was 100 kHz, the insweep frequency was 200 kHz, the step size is 100kHz, thus we have overlapping slices. The transmitted power was ~2 Watt. The acquisition time was 1 second. The pulse delay was 10 seconds. The median resonance frequency was 183.4 MHz, the gradient strength was 310 T/m. As quantitative indication, a SNR<sub>time</sub> was calculated from the MRFM time signal by dividing the maximum, real voltage by the standard deviation from the imaginary signal.

The delay was relatively short, only 10 seconds (~ 2·T<sub>1</sub>). Eq. 5.27 predicts for detection of the entire sample a single shot SNR of 88 and a maximum force of 59 fN for T<sub>lim</sub> = T<sub>1ρ</sub> = 1 second. The observed maximum force value of ~10 fN is about 1/6 of this, which is reasonable considering the fact that we did not acquire the full signal. The acquisition time was too short and the mentioned total force represents the sum of the contributions from about five slices. Furthermore, the lock-in time constant was set too short (τ<sub>L</sub> = 0.1 s), thereby increasing the noise and the SNR decreased with a factor of √T<sub>lim</sub>/τ<sub>L</sub> = 3.3. An RF power meter was placed after the RF passed through the coil, before the resistive load. The readout of the power meter showed a constant power, indicating that the stability of the applied RF power was reasonable. The transmitted power remained around 2 Watt during these experiments. The gradient drift was estimated to be less than ±1 μm per day and the fiber optic sensitivity was determined by the lateral μm x-y alignment of the fiber end and the cantilever. The stability of the optical sensitivity was irregular. In MRFM design I, sometimes, the optical alignment could get completely lost after time or after a wild cantilever oscillation, other times the sensitivity would fluctuate only < 10% within one day.

The calculation of the number of spins from the magnitude of the force in a slice can introduce additional differences in relative intensities, due to differences in measured S, Q, T<sub>1ρ</sub>, see Eq. 5.39 and figure 7.6c.

### 7.4 Practical MRFM example IV - AlGaAs 5 μm thin film

In collaboration with C. Degen and B. Meier at the ETH in Zürich, MRFM data was acquired from their setup for AlGaAs samples in a 6.0 Tesla magnet (ν<sub>H</sub> = 250 MHz). Very sensitive cantilevers, see figure 7.7, were produced by Schahrazede et al. [165] from the laboratory of micro systems, EPFL in Lausanne, Switzerland. The minimum detection limit that can be reached with such cantilevers in comparison with the commercial cantilevers from Veeco (SiN, k<sub>e</sub> =0.01 N/m) is about 10 times
Table 7.2: Overview of the $T_1$ relaxation times from Ref. [42] and the determined $T_{1p}$ relaxation times of the nuclei in AlGaAs. Courtesy of C. Degen.

<table>
<thead>
<tr>
<th>nucleus</th>
<th>$T_1$ (ms)</th>
<th>$T_{1p}$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{27}$Al</td>
<td>16000</td>
<td>1100±100</td>
</tr>
<tr>
<td>$^{71}$Ga</td>
<td>770</td>
<td>430±20</td>
</tr>
<tr>
<td>$^{69}$Ga</td>
<td>290</td>
<td>230±20</td>
</tr>
<tr>
<td>$^{75}$As</td>
<td>200</td>
<td>195±25</td>
</tr>
</tbody>
</table>

lower. The other noise sources should be low enough to work with these sensitive cantilevers. It was observed for example in MRFM design I that these cantilevers were kept in resonance, either by weak vibrations or by the laser power. The mounting of the sample and placement in the setup was more difficult due to the increased floppiness. With this cantilever it was possible to obtain an MRFM signal with decent SNR of all the nuclei in AlGaAs (see figure 7.8 and table 7.2). Of course, the Arsenic signal had the lowest SNR. In 2013, the $^{69}$Ga MRFM signal from GaAs was measured at 5 Kelvin with the gradient on cantilever approach by Alexson et al. [166].

Figure 7.7: The cantilevers had a length of 500 $\mu$m, a width of 10$\mu$m and a special optical panel. The Q factor of this cantilever in the setup was ~8.000, while maximum Q factors of 50.000 were achieved. The spring constant was $k_c = 0.11$ mN/m. In these figures, an AlGaAs sample of 40x50x5 $\mu$m was glued on top.

In Al$_{0.5}$Ga$_{0.5}$As, the $^{75}$As rotation pattern of the central transition of the second order quadrupolar interaction ($\sim$ 33 MHz) extends over ±2 MHz (see Section 3.3). At 6.0 Tesla, this range increases to ±4.8 MHz. In a $^{75}$As MRFM measurement with 2000 averages, we did notice systematic signal contribution in the range of -1.0 to 0 MHz (the blue spot in figure 7.9). However, the time-domain of these signals show that this "sinus" like shape does not correspond with a real MRFM spin signal. This signal lasts very short and it looks more like an artefact from the closed loop functionality or a low frequency vibration / RF disturbance. Therefore, we did not see any contribution from a different Arsenic site within the scan range of ±1.0 MHz (see figure 7.9). However, it is likely that we did not scan wide enough to observe these sites. The $^{75}$As signal displayed here could originate solely from the As[Ga] and the As[Al] sites.
Figure 7.8: \( T_{1\rho} \) fits of all the nuclei in Al\(_{0.5}\)Ga\(_{0.5}\)As. The lock-in time was set to 30 ms, the \( Q_{\text{closed}} \) = 20. The pulse delay was 4 seconds for Al and \(^{69}\)Ga, the insweep frequency was 250 kHz, the sweep full amplitude was 150 kHz, the frequency step size was 400 kHz. The pre-heating time was 0.2 s, the acquisition time is displayed on the horizontal axis. The cantilever frequency was relatively low, 328 Hertz.

7.5 Theoretical MRFM example V - AlGaAs 1 \( \mu \)m thin film

Suppose we want an \(^{75}\)As image of a Al\(_{0.5}\)Ga\(_{0.5}\)As thin film of 10x10x1.0 \( \mu \)m, with a z-spatial resolution of 100 nm at room temperature. The mass of this sample is only 0.5 ng, calculated with the GaAs mass density of \( \rho = 5.3 \text{ g/cm}^3 \). If we have a commercial cantilever with \( k_c = 0.01 \text{ N/m} \) and \( Q = 10000 \), the empty resonance eigen-frequency of 7.2 kHz will hardly change because of this low mass. At a lock-in integration time of 1 second, the detection limit is 0.25 nT. The \(^{75}\)As spin density in Al\(_{0.5}\)Ga\(_{0.5}\)As is 8.1 mol/kg. The sample contains \( 2.6 \cdot 10^{12} \) As spins. The magnetic moment of one As spin at 293K, \( B_0 = 4.3 \text{ T} \) is \( 1.3 \cdot 10^{-32} \text{ Am}^2 \). At a gradient magnetic field of 1000 T/m, this would create a force of \( 1.2 \cdot 10^{-14} \) nN per As spin, corresponding to a single shot SNR of 0.12, if we would detect all spins in the entire sample. If we want to achieve a SNR of 10, about 7000 scans are needed. If each scan would take \( \sim 5 \) seconds, the experiment will take about 10 hours, which is reasonable.

A 100 nm thick slice would have 10 times less spins. To obtain a similar SNR from this slice would take 100 times longer, which is 40 days per slice. To scan the ten slices would take 1 year and to also search for the signal would take much too long. The stability of the MRFM design becomes more important for longer measurements. In fact, the real SNR is even lower because of a low \( T_{1\rho} \) and a narrower PSF. Filling in Equation 5.27, with \( T_{1\rho} = T_{\text{lim}} = 0.2 \) s, see table 7.2 and with an effective PSF width of 0.8 x 760 Hz = 600 Hz, we loose another factor of 11.
Figure 7.9: (upper) $^{75}$As MRFM time signals from 2000 scans. (lower) The corresponding integrated image. No other Arsenic sites were observed. $f_c = 323$ Hz, $Q = 5300$, $Q_{closed} = 20$. The center frequency was $\omega_R = 256.1$ MHz, $\omega_{As} = 43.793$ MHz, pulse delay is 0.2 seconds, 40 frequency steps were made with an interleaving of 2. The step size was 300 kHz, the pre-heating time was 0.1 second.

Thus, this experiment should be done preferably at a lower temperature. At 3.0 Kelvin, the temperature is approximately a factor of 100 lower, the magnetic moment is roughly a factor 100 stronger and the noise is 10 times lower, increasing the SNR by a factor 1000. Thus, we can detect about $10^6$ less spins. The measurement of 10 slices with 100 nm height can then be recorded in 5000 seconds. The detection limit is much lower 0.03 fN, corresponding to a positional displacement noise of only $S_u = 0.0018$ pm$^2$/Hz for $Q_{closed} = 10$. The vibration isolation and the optical detection needs to be improved. The complete design should be able to operate at these low temperatures. The z-spatial resolution is blurred by the PSF and the gradient field profile. For enhanced spatial resolution, the RF sequence of Section 8.4 can be used. A good, gradient profile can be generated with a big cylindrical rod. Since the radius of a rod is much bigger than the lateral sample dimensions, the magnetic field is expected not to change much over the height. The center resonance frequency is $\sim 32$ MHz. The resolution is 7.6 kHz/µm. The full sweep amplitude for a 100 nm slice is only 760 Hz, thus the $B_1$ field can be chosen small. A 50 µm wire with 5 turns and a power of 0.75 Watt, at 100 µm distance from the edge of the coil, can generate an RF field of 20 kHz, so that the adiabaticity is sufficient, $A \sim 3.6$. 
Chapter 8

MRFM Spin Manipulation

As described by Degen and Verhagen, the MRFM pulse or waveform sequence generally starts with a spin excitation part followed by a spin detection part. In this chapter different sequences (e.g. ADRF and ADLF) are applied to obtain an increased SNR with respect to the standard MRFM detection algorithm. Furthermore, other sequences are used to determine the RF field strength, to generate a narrow band detection profile, or to gather more information about the spin system, i.e. dipolar coupling, polarization transfer coefficients, relaxation or diffusion constants. The diverse sequences and approaches illustrate the wide range of applications for MRFM besides imaging.

8.1 Interleaved frequency stepping

Interleaving is a way to re-arrange data in a non-contiguous way. It is used for example in computer science, i.e. data storage, multimedia file formats and transmission of (burst) signals. It is also used in magnetic resonance imaging. Degen et al. showed that it can be used in MRFM to decrease the scan time of an image [65]. This is especially favorable when the spin-lattice relaxation time is long and the image is build up out of many slices. After the acquisition, the interleaved slices are repositioned, so that the image is reconstructed with the corrected linear frequency scale. For each experiment, the interleave spacing can be chosen. For example when the interleaved spacing $n = 2$, 10 slices are recorded as 1, 3, 5, 7, 9, 2, 4, etc.

8.2 Nutation

In a nutation sequence the length of the RF pulse increases linearly with each next measurement. In MRFM, the amplitude of the RF pulse can be different than the amplitude of the detection, see figure 8.1. To generate short, high power pulses, a BLAX1000 amplifier is connected. The 300W output channel of this amplifier is better protected against reflected power than the 1000W output channel. Furthermore, we determined experimentally that without sending any power, the 300W
channel generated less noise artefacts than the 1000W channel. These noise artefacts were picked up by the cantilever and could originate for example from different internal grounding of the amplifier for each channel. For low power FAPs we used the BLAX 5, which had sufficient power and is even more resistant to the reflected RF power than the 300W channel of the BLAX1000, under the relatively long irradiations. The maximum achieved RF field, measured with MRFM, for a $Q \approx 1$ resonator, is $\sim 60$ kHz at 7 Watt (pulse) power. The RF field strength is proportional to $x^{-1}$, where $x$ is the distance to the center of the sample and the center of the micro-coil. The micro-coil wire diameter is $50 \mu$m and the coil had a length of $\sim 300 \mu$m. The sample is $\sim 200 \mu$m away from the center of the coil and thus only $50 \mu$m away from the edge of the coil.

### 8.3 Hahn-echo

In MRFM, it is possible to combine imaging with low resolution spectroscopy. In this manner, the possibility to retrieve the dipolar interaction with MRFM is demonstrated by Degen et al.\cite{degen2012hahn}

For MRFM 'spectroscopic' experiments Hahn-echoes can be particularly useful, since these echoes refocus the dispersion of the signal caused by the strong gradient field inhomogeneity. A Hahn-echo refocuses the magnetization from the spin ensemble in the transversal plane. The following sequence is investigated, see also Ref. \cite{degen2012hahn} 'echo spectroscopy'. The MRFM Hahn-echo pulse sequence is

$$90_{\pm x} - \frac{t_1}{2} - 180_{-y} - \frac{t_1}{2} - 90_{\pm x} - \text{detect}M_z$$

, where the detection of the macroscopic longitudinal magnetization in a slice, $M_z$, occurs via the conventional two step $\pm I_z$ spin temperature cycling (see section 7.1.3). First, a 90 degree pulse is
8.4 A NOVEL DETECTION SEQUENCE

Figure 8.2: $^1$H MRFM Hahn-echo of ammonium sulfate. $\nu_F = 180.8$ MHz, acquisition time is 2 seconds, 32 averages, sweep half-amplitude $= 80$ kHz, off-resonance frequency is 1 MHz, pulse delay is 30 seconds, the $t_1$ increment is 4 $\mu$s. The pre-heating time is 0.2 seconds. The 90 respectively 180 degree pulse times were 5 and 14 $\mu$s. Total acquisition time is $\sim$6 hours. (left) integrated time signal. (right) Fourier transformed signal and fit with a Gaussian with a FWHM of 48 kHz.

given and then a 180 degree pulse, placed in between two delays. The spin-echo 180 degree pulse selectively refocuses the effect of the magnetic field inhomogeneity, but not of the dipolar couplings. It is verified that each MRFM phase-cycling step functioned properly by checking the phase of the MRFM signal. A nutation spectrum is obtained to determine the 90 and 180 degree pulse times. The bias in the nutation, is in this pulse sequence, compensated by the phase-cycling, resulting in a zero signal at long $t_1$ times (see figure 8.2). We determined a FWHM of 48 kHz at 4.3 Tesla. Degen et al. found a smaller FWHM of $\sim$20 kHz at 6.0 Tesla. Their longer lasting time signal is attributed to a more homogeneous, higher RF field, at a closer distance to the micro-coil. The use of optical triangulation in their setup, allowed the sample to be placed closer to the center of the micro-coil. A maximum RF field of 170 kHz[65] has been used in an MRFM setup using optical triangulation. In MRFM design I and II, the fiber is positioned next to the micro-coil, which means that at least the radius of the fiber ($125 / 2 = 62.5$ $\mu$m) is extra distance between the sample on the cantilever and the coil, which significantly reduces the RF field strength.

This type of MRFM Hahn-echo measurements could be applied in chemical contrast imaging. Besides the information in the image, additional spectral information about the selected slice in the sample by adding a dimension in $t_1$. Besides dipolar information also for example quadrupolar information could be retrieved with the Hahn-echo. The Hahn-echo sequence can be extended to select a certain coherence path-way[167]. If sufficient RF field strength is available to excite/detect the satellite transitions, such a scheme is useful for spectrally resolving quadrupolar echoes in the $t_1$, spectral dimension.

8.4 A novel detection sequence

As is described in Section 5.9, the detected MRFM signal originates from a convolution of the magnetization from the spins in the resonant slice with the detection function. What happens during the MRFM detection period is important, it clearly consumes the most time, typically a
few seconds, while the excitation only takes a few milliseconds or less. The detection wave-sequence determines the frequency detection profile, which is responsible for the shape of the resonant slice used in the detection phase. Different detection waveform functions, such as ramped, linear sawtooth, sawtooth 180 degrees, etc. were proposed and analyzed by Degen et al.

Here, a novel detection sequence is described that can be used for narrow-band detection purposes like spin diffusion or high spatial resolution imaging. In these cases, it is important to detect a rather well defined, rectangular, thin slice. A novel waveform is constructed by a slight modification of the commonly used sawtooth/triangular function. This has a strong effect on the detection profile, while at the same time it is not generating additional spurious cantilever noise. The frequency $\omega_1(t)$ and the phase dependency $\phi_1(t)$ of a conventional, linear sweep $A_1(t)$ can be written as

$$\omega_1(t) = \omega_{ampl}(1 - 2t/\tau_{swp}) \quad (8.1)$$

$$\phi_1(t) = \int \omega_1(t) dt \quad (8.2)$$

$$A_1(t) = aX \cos(\alpha + \phi_1(t) + \omega_{carrier} t) \quad (8.3)$$

for $t = 0...\tau_{swp}/2$, with $\tau_{swp}$ the sweep time, $\omega_{ampl}$ the sweep amplitude, $aX$ the amplitude, $\alpha$ the start phase and $\omega_{carrier}$ the waveform carrier frequency. By looking closely at the phase dependency $\phi_1(t)$, it resembles a sinus function. By implementing the frequency sweep $A_2(t)$ using phase modulation of the carrier, the resulting spatial slice selection profile (PSF) is significantly sharper (see figure 8.3).

$$\omega_2(t) = \frac{d\phi_2(t)}{dt} \quad (8.4)$$

$$\phi_2(t) = \frac{\tau_{swp}}{8} \omega_{ampl} \sin\left(\frac{2\pi t}{\tau_{swp}}\right) \quad (8.5)$$

$$A_2(t) = aX \cos(\alpha + \phi_2(t) + \omega_{carrier} t) \quad (8.6)$$

### 8.5 Adiabatic De-and (Re-)magnetization in the Rotating Frame

In 2008, Lin and Eberhardt et al. showed that it is possible to do magnetic double resonance force microscopy[17, 134] using Hartmann-Hahn matching on two RF channels. In theory, the enhancement of the polarization via the transfer of dipolar nuclear magnetization should also be possible in MRFM. The main advantage of this transfer is that sequentially, only one active RF channel is needed and the rather sensitive Hartmann-Hahn condition is avoided. In regular NMR it has been shown that such transfer can be achieved by sequentially storing and collecting the magnetization via the dipolar reservoir using Adiabatic De-and (Re-)magnetization in the Rotating Frame (ADRF/ARRF). ADRF is first described by Slichter et al.[18] in 1961, who used the representation from Redfield[168] (1955) of a thermal reservoir representing the energy of a system with two unlike nuclear spins.
8.5. ADIABATIC DE-AND (RE-)MAGNETIZATION IN THE ROTATING FRAME

Figure 8.3: (left) The frequency offset, labeled $\omega$ and the phase labeled $\phi_1, \phi_2$ of the linear sweep ($1 =$ dotted line) and the improved sweep ($2 =$ solid line). The functions are mirrored around half the period $\tau_{sup}/2$. (right) The corresponding simulated PSF during the detection period, $\omega_{carrier} = 2\pi \cdot 10$ MHz. The jumps/spikes in the PSF were also observed in the experimental spectrum, obtained with a spectrum analyzer. They originated from the limited time increment of 25 ns of the 40 MHz waveform generator board.

8.5.1 Theory

In a simplified two spin system, with dominant spin $I$ and rare spin $S$, the time-dependent Hamiltonian for a two spin $\frac{1}{2}$ system is

$$H_{\text{tot}}(t) = H_{rf} + H_d + H_z$$

(8.7)

By switching to a resonant frequency reference frame at $H_z$ (which includes the frequency offset from the gradient), the Hamiltonian is truncated. The hetero-nuclear coupling $\omega_{IS}$ is the relevant dipolar coupling needed for the transfer of the polarization from the two spin species,

$$H_{\text{ref}}(t) = \omega_{\text{nut}}(t) I_x + \omega_{IS} 2 I_z S_z$$

(8.8)

The effective field strength and its angular variation in the rotating frame can then be written as

$$\omega_{\text{eff}}(t) = \sqrt{\omega_{\text{nut}}^2 + \omega_{IS}^2}$$

$$\theta = \arctan \left( \frac{\omega_{IS}}{\omega_{\text{nut}}} \right)$$

(8.9) (8.10)

The ramping of the amplitude should be done adiabatically, i.e. $A >> 1$ or

$$\frac{\partial \theta}{\partial t} \ll |\omega_{\text{eff}}(t)|$$

(8.11)

Substituting this equation and integrating over the duration time of the ADRF $\tau$ yields,

$$\omega_{\text{nut}}(t) = \frac{\omega_{IS}^2 (\tau - t)}{\sqrt{A^2 - \omega_{IS}^2 (t - \tau)^2}}$$

(8.12)

Re-writing terms and substituting $\omega_{\text{nut}}(0)$ gives

$$\omega_{\text{nut}}(t) = \frac{\omega_{\text{nut}}(0) \omega_{IS} (\tau - t)}{\sqrt{\tau^2 \omega_{IS}^2 + \omega_{\text{nut}}(0)^2 (2\tau - t)}}$$

(8.13)
Figure 8.4: (a) The cubic KPF₆ at ambient temperature. The purple (darkest) atoms, on the center of the axis of the cube, are potassium, the orange (lighter) atoms, on the outer fcc lattice, are phosphorus and the green (lightest) atoms, in groups of six, are fluorine. The lattice constant is 7.789 Å [169]. The symmetry group is FM3-M. The closest distance in this lattice is the distance from fluorine to phosphorus, which is 1.5946 Å. This image is obtained from the ICSD [170]. (b) The RF circuit. A BLAX 5 Watt amplifier is used. The ¹⁹F band pass filter ranged from 165-185 MHz, and the ³¹P filter from 60-85 MHz. A micro-coil in the probe is connected to a broadband transmission line with a 50 ohm load. The micro-coil had an outer diameter of 300 µm and 4 turns of 50 µm copper wire.

The combination of the selected duration time of the ADRF, the maximum RF field strength and the dipolar coupling determines the adiabaticity.

\[ A = \omega_{IS} \cdot \tau \frac{\omega_{IS}^2 + \omega_{nul}^2(0)}{\omega_{nul}(0)} \]  \hspace{2cm} (8.14)

\( \omega_{IS} \) is defined as

\[ \omega_{IS} = \frac{b_{IS}}{2} (3 \cos(\theta_B)^2 - 1) \]  \hspace{2cm} (8.15)

with \( b_{IS} \) the magnitude of the hetero-nuclear dipolar coupling and \( \theta_B \) the angle with respect to \( B_0 \). Since the hetero-nuclear coupling is small, the adiabatic condition is easily fulfilled. In MRFM off-resonance sweeps are needed to transfer magnetization within the relevant spatial region. The sweep off-resonance frequency can be considered in the Hamiltonian (\( \Omega_L \)). In fact, this will increase \( \omega_{nul} \) and simplify the adiabatic condition.

### 8.5.2 Experimental

KPF₆ is chosen for its favorable MRFM properties \( (T_{1,p} > 1s, 1s < T_1 < 60s) \) [17, 134]. The K and P atoms of cubic KPF₆ occupy the same positions as Na and Cl in the rock-salt structure-type, see figure 8.4a. The sample dimensions were approximately 40 x 50 x 50 µm. The frequency of the RF channel could be switched by using hardware latches in the PTS. The latches could be set
with the PC in advance, so that during waveform generation, they could be switched rapidly. The timing of the waveform generation is synchronized with the two onboard PC hardware counters. The minimum switch time is limited by the counter time of the IO-board, i.e. 2 times the reciprocal value of the cantilever frequency. In this case \( f_c \) is 1160 Hz and the switch time \( \approx 2 \) ms. The RF circuitry is shown in figure 8.4b. The minimum detectable force is 0.75 fN \((\approx 1.5 \times 10^{13} \text{ Fluor spins})\) (no averaging), for a lock-in integration time constant of 1 second. The KPF\(_6\) sample had a mass of 190 ng, which contained \( \approx 3.7 \times 10^{15} \) F spins and \( 6.2 \times 10^{14} \) P spins. Due to limited RF field strength, it is not possible to detect all spins in the sample, but the slice volume is limited to maximal \( \approx 1/3 \) of the volume, at a magnetic field gradient of \( \approx 1200 \text{ T/m} \). A typical, large, \(^{19}\text{F}\) full-sweep amplitude is 800 kHz. The full MRFM signal width extended over 2.4 MHz. For \(^{31}\text{P}\) the full sweep amplitude is 350 kHz and the signal width is about 1 MHz. The \(^{19}\text{F}\) signal could be detected in a single scan with a SNR of \( \approx 15 \), but the \(^{31}\text{P}\) signal required a minimum of 8 scans. With nutation, an RF field of 46 kHz is determined, at 1 Watt of transmitted power and \( \nu_F = 171.1 \) MHz. The \(^{31}\text{P}\) RF field strength is approximated with the gyro magnetic ratios \( \approx 20 \) kHz, hereby neglecting the self-inductance of the micro-coil.
**Figure 8.5:** (left) The MRFM sequence to determine the $T_{1d}$ relaxation times. (right) Plot of the time dependency of the normalized, integrated magnetization. A normalization is made with respect to a direct experiment, where the pre-detection sweep starts from the insweep frequency to half the sweep amplitude. The acquisition time is 3 seconds. The pre-time is 2 seconds and the sweep time (swtm) is 5 ms. The ADRF/ARRF profile is determined on the basis of $\nu_{tmin} = 20$ kHz, $\nu_{IS}=5$ kHz and $\tau = 1$ ms, giving an adiabaticity $> 30$. The transmitted power is 1 Watt. The gradient strength is around 1200 T/m. The improved, sharp PSF detection profile (see Section 8.4) is used. $T_{1d}^F$: The center resonance frequency is 176.3 Mhz. The pulse delay is 20 seconds. The signal is averaged over 2 scans. The full sweep amplitude is 320 kHz and the insweep frequency 200 kHz. $T_{1d}^P$: The resonance frequency is 76.1 Mhz. The pulse delay is 90 seconds. The signal is averaged over 16 scans, the insweep frequency is 120 kHz and the full sweep amplitude 160 kHz.

<table>
<thead>
<tr>
<th></th>
<th>$^{19}$F</th>
<th>$^{31}$P</th>
</tr>
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<tbody>
<tr>
<td>$T_1$ (s)</td>
<td>6.2±0.7 [171]</td>
<td>≈ 30 [171]</td>
</tr>
<tr>
<td>$T_{1d}$ (s)</td>
<td>5.9±0.4</td>
<td>3.6±1.3</td>
</tr>
<tr>
<td>$T_{1P}$ (s)</td>
<td>5.2 [171]</td>
<td>2.7 [171]</td>
</tr>
<tr>
<td>$\omega_D$ (kHz)</td>
<td>20 [65]</td>
<td>1.5 [17]</td>
</tr>
</tbody>
</table>

**Table 8.1:** Summary of the experimentally determined relaxation times of KPF$_6$. For both nuclei, the relation of $T_{1P} < T_{1d} < T_1$ is valid. Based on the internuclear distances, the heteronuclear PF second moment would be $\sqrt{(\langle M^2 \rangle)} = 78$ kHz. Since the PF$_6^-$ groups can rotate freely, the hetero-nuclear coupling is strongly reduced. The hetero-nuclear PF coupling is assumed to be $\nu_{IS} < 5$ kHz.

### 8.5.3 Dipolar reservoir relaxation

To verify that the dipolar reservoir relaxation times were sufficient, the $T_{1d}^F$ and $T_{1d}^P$ were determined. The sequence is described on the left side of figure 8.5. After the cantilever pre-heating time (pre-time), the magnetization is swept from insweep to on-resonance, refocusing the magnetization from the entire sample. The spins are then locked in the rotating frame and undergo ADRF. A variable delay time is implemented between the ADRF and the ARRF. Using ARRF, the magnetization is
recalled from the dipolar reservoir, after which the detection period follows. The obtained $T_{1d}^F$ values are listed in table 8.1. The $T_{1d}$ value is much closer to $T_1$ for fluorine than for phosphorus, which might be explained by the fact that there are relatively much more fluorine than phosphorus atoms in KPF$_6$. Since both $T_{1d}$ decay times were in the order of seconds, and the hetero-nuclear dipolar coupling is relatively small, favorable conditions are expected for the transfer of nuclear polarization. Because of the long $T_{1ds}$, the signal loss due to the 2 ms switch time is negligible.
Figure 8.6: (left) The different waveform sequences in the frequency domain are shown. ADRF storage occurs where there are is one ‘storing’ sweep and one recalling sweep follows. A reference experiment does not contain any pre-sweeps, but does have the pre-heating time at a fixed frequency. F=Fluor, P=Phosphor, c=centered, fixed frequency, i=interleaved scanning. The interleaved scanning on the Fluor channel has an interleaved spacing of \( n = 4 \). The frequency steps were \( f_{\text{step}} = 400 \) kHz, insweep amplitude = 180 kHz and sweep half-amplitude 160 kHz. Experiment I to IV is done with 1, 2, 2, 8 averages. The frequency switch time from P to F is 2 ms. In experiment II the ADRF time is 3.2 ms and \( \nu_1 = 50 \) kHz. In experiment III the ADRF time is 7.2 ms and \( \nu_1 = 22 \) kHz. (right) The graphs display the real, integrated voltage of the MRFM scans.

8.5.4 Adiabatic De- and Re-magnetization in the Rotating Frame

Four experiments were done with the ADRF/ARRF sequence under MRFM. Because the SNR of the \(^{31}\text{P}\) MRFM image is weak, it is decided to monitor the loss of signal in the \(^{19}\text{F}\) MRFM image. Thus, the polarization transfer efficiency ratio is determined from the ratio of the original \(^{19}\text{F}\) signal and when the polarization transfer occurs from \(^{31}\text{P}\) to \(^{19}\text{F}\), see figure 8.6. In the first experiment, the \(^{19}\text{F}\) graph displays a direct image, without ADRF/ARRF. Second, the \( F_{\text{ref}} \) dotted line shows a reference image. In this experiment, the Fluor signal is constantly stored in the dipolar reservoir with ADRF in the central slice. The detection occurs by interleaved scanning in combination with ARRF. Only when the storing and recalling frequencies match, at the central slice, there is a strong Fluor signal. In the other slices, no background Fluor signal is observed. The intensity from the central scan is almost equal to the first, direct scan. In the third experiment, the \(^{31}\text{P} \leftrightarrow \) \(^{19}\text{F}\) image displays the transfer via the hetero-nuclear dipolar reservoir, the Phosphor storing and Fluor recalling frequencies are both scanned interleaved. Because the second scan does not show any off-center intensity, the signal must originate from the transferred polarization from Phosphor. The integrated ratio of all scans is 0.41, while \( \gamma_\text{P}/\gamma_\text{F} = 0.43 \). Therefore, the polarization transfer from Phosphor to Fluor is 95% efficient. The \(^{31}\text{P}\) MRFM signal is shown in the lower part of figure 8.6 (experiment IV).
8.5.5 Adiabatic De- and Re-magnetization in the Laboratory Frame

While CP and ADRF can achieve moderate enhancement factors (here $\gamma_F/\gamma_P$), a relatively new approach is called Adiabatic Demagnetization in the Laboratory Frame (ADLF). Lee et al.\cite{172} have shown theoretically and experimentally in regular NMR, that this technique can obtain higher enhancement factors by transferring polarization via the Zeeman reservoir. An additional gain of $\sqrt{(N_I/N_S)}$ can theoretically be obtained, where the $N_I$ spins are abundant and the $N_S$ spins rare. Lee et al. studied this effect by applying long, $\sim 100$ ms, single sweeps.

In the pulse sequence shown in Figure 8.7, the spins in a certain slice are swept from the +insweep frequency to on-resonance. Then, the amplitude is adiabatically ramped to zero. In this process the Zeeman order is transferred to Dipolar order. Then, on the frequency of the $^{31}$P channel, the Dipolar order is transferred to Zeeman order and this signal is measured via FAP's. ADLF is interesting for MRFM, since frequency sweeps are used for detection/excitation and the MRFM setup is static (no MAS), as this type of transfer only works statically and requires relatively long $T_1d$'s. Five experiments were done to investigate the applicability of the ADLF/ARLF sequence in MRFM (see figure 8.7). The only difference with the sequence described in figure 8.5 is that the ADRF/ARRF amplitude ramping part is now removed. Again, because of the weak $^{31}$P MRFM signal, we observe the ratio in the $^{19}$F MRFM signal of a normal scan and a scan where we transfer the polarization from $^{31}$P to $^{19}$F. The signal strength should be reduced from 1.0 to the gyromagnetic ratio $\gamma_P/\gamma_F = 0.43$ divided by $\sqrt{(N_F/N_P)} \approx 2.45$ is 0.18.

Experiment I displays the direct Fluor signal, in which the maximum intensity is normalized to 1. In experiment II the storing of spins in the Zeeman reservoir always occurred at the center frequency. Again a strong signal is observed when the storing and recalling frequencies matched, like in the ADRF/ARRF experiment. Although the same frequency spacing of 400 kHz and the same slice height of 2 x insweep = 360 kHz $\equiv$ 17 $\mu$m were used as in the ADRF experiment, a -0.19 minimum value of the integrated MRFM signal is observed in neighboring slices around the central frequency. The detection in experiment II occurred directly after a sweep, while the ADRF sequence had a constant frequency and only amplitude ramping, both during a few milliseconds. The signals at each side of the center are attributed to the frequency sweep in the ADLF, which affects the magnetization across the slices much stronger than the sweep followed up by amplitude ramping in the ADRF sequence. Experiment III had the weakest signal, however, theoretically no signal is expected. The 8% F signal is considered a background Fluor signal, since, although the frequency sweeps start in the center during the detection phase of experiment III, some of the Fluor spins at this central, interleaved, detection frequency can be inverted by the CW irradiation at the insweep Fluor frequency. In experiment IV, an additional 4% increase is observed, when the frequency is switched to the $^{31}$P frequency first. In experiment V the Fluor polarization is enhanced from 12 to 22%. The theoretical reduction of $43%/2.45 = 18\%$ is close to the experimentally measured, integrated value. The amount of spins which remain locked in the detection slice determines the signal amplitude and enhancement.
Figure 8.7: (left) The different waveform sequences in the frequency domain are shown. ADLF storage is displayed by two convergent sweeps. The negative sweep in the first scan and the positive sweep in the second. A reference experiment does not contain any pre-sweeps, but does have the pre-heating. F = Fluor, P = Phosphor, c = centered, fixed frequency, i = interleaved scanning. The detection occurred interleaved on the Fluor channel, with an interleaved spacing of $n = 4$. (right) The corresponding integrated, normalized, real MRFM signals. The acquisition time is 3 seconds and the repetition delay is 3 seconds. The frequency steps were $f_{\text{step}} = 400$ kHz, insweep amplitude $= 180$ kHz and sweep half-amplitude $160$ kHz. The active Fluor slice height of $\sim 17 \mu m$ corresponded to a Phosphor insweep amplitude of $77$ kHz. The $^{31}P$ step size is $172$ kHz. The sweep time is 20 milliseconds and the pre-heating time is 1 second, in all five experiments. A two step, spin temperature $\pm 1_2$ phase-cycling is used. All experiments had 4 averages. The gradient field strength is 1240 T/m.

8.5.6 Conclusions

The transfer of polarization in KPF$_6$ using MRFM is investigated. Because the $^{31}P$ MRFM signal is relatively low, all readouts occurred on $^{19}F$. With ADRF/ARRF it is possible to observe the reduction in dipolar polarization when the polarization is transferred from phosphorus to fluor. The measured, integrated ratio of all scans is 0.41, while $\gamma_P / \gamma_F = 0.43$. Therefore, the polarization transfer from Phosphor to Fluor is 95% efficient. In the ADLF/ARLF scheme, the measured, integrated reduction in Fluor polarization is 22% close to $(\gamma_P / \gamma_F) \cdot \sqrt{(N_P / N_F)} = 18\%$. However, the ADLF/ARLF scheme is less selective than the ADRF/ARRF scheme and has more issues with background signals and unwanted signal from adjacent slices. Further research is needed to understand why the direct enhancement of polarization on the Phosphorus MRFM signal is not observed.

Theoretically, the Phosphorus polarization enhancement with ADLF/ARLF could reach up to 2.32 x 2.45 = 5.7 times. The methods could be extended to quadrupolar nuclei, as it has been done in regular NMR[173, 174]. Furthermore, it could be used to apply chemical contrast in MRFM images as in [3, 65]. Since the electronic circuit in MRFM is often used with a low Q factor and a wide frequency range, it is suited for magnetization transfer for a wide range of nuclear spins, with an advantage over CP that with long dipolar/Zeeman relaxation times only one RF channel is needed for the generation in a sequential mode. The ADRF/ARRF ADLF/ARLF sequence could also be
used to only *select* the (homo- or hetero nuclear) dipolar or Zeeman Hamiltonian.
Chapter 9

Real-Space Spin Diffusion (a feasibility study)

9.1 Introduction

Spin diffusion is a well-known process in which magnetization can be exchanged spontaneously over time. The transfer is associated with flip-flops caused by the dipole-dipole exchange interaction allowing the spins to continuously exchange polarization in an energy-conserving way. In conventional NMR, spin diffusion in solids can be measured using pulsed field gradient spin echoes[175, 176]. The direct measurement of spin diffusion in real space is challenging since it requires the detection of polarization changes within a small diffusion length of \( \sqrt{2DT} \)[175] during \( T_1 \). It is difficult to capture the direct, real-space spin diffusion since most materials have a relatively slow spin diffusion constant in the range of \( D \sim 10^{-12}...10^{-10} \) cm\(^2\)/s resulting in only sub \( \mu \)m displacements during \( T_1 \).

In standard NMR systems normally a z-coil is present that can generate adjustable magnetic z-gradient fields up to about \( \sim 50 \) T/m. Normally, spin diffusion is observed with the following method[175]. First, a z-gradient pulsed field is applied, which creates an initial, inhomogeneous magnetization grating throughout the sample. The grating originates from the differential rates of spin precession for spins at different spatial offsets in the linear magnetic field z-gradient. Then, spin echoes are employed to manipulate, i.e. store and restore the magnetization in a certain plane of preference, after a time the magnetization is restored with an inverted z-gradient pulse and detected. From the decay of the magnetization, the spin diffusion constant can be derived.

When the detectable spin diffusion travels over long distances, for example in materials with very long \( T_1 \)'s such as CaF\(_2\)[177, 175], a low spatial resolution can suffice. In materials with shorter relaxation times and/or lower diffusion constants, a higher spatial resolution is necessary. Since the spatial resolution is proportional to the magnetic field gradient, conducting the experiment in a much stronger gradient magnetic field is needed. MRFM facilitates solid-state NMR measurements at very strong, constant magnetic field gradients. Because the field gradient is constant, this allows the direct detection of the spin diffusion in real-space. In 2004, Budakian et al.[178] showed that the paramagnetic electron spin diffusion can be suppressed with MRFM by means of a strong gradient
of 15 kT/. The reduction of the electron spin diffusion in turn reduced the spin-lattice relaxation time. The direct detection of $^{19}$F real-space spin diffusion at gradient fields of $\sim 4$ kT/m with MRFM in CaF$_2$ has been demonstrated in 2007[179]. Eberhardt et al. determined diffusion constants of $D_d = 11 \pm 11 \cdot 10^{-12}$ and $D_Z = 6.2 \cdot 10^{-12}$ cm$^2$/s in CaF$_2$[179].

In this study we analyze the direct, spatially resolved detection of $^{19}$F spin diffusion in KPF$_6$ with Magnetic Resonance Force Microscopy at a magnetic gradient field around 1 kT/m. Since the shortest atom to atom distance in the KPF$_6$ lattice is 1.6 Å and fluor dipolar couplings are in the order of 10 kHz, $B_d \approx 2$ mT, $\nabla B \cdot a \ll B_d$. In this context the spin diffusion is merely reduced because of the presence of the gradient magnetic field. The strong gradient magnetic field in MRFM causes the relaxation and the diffusion to be interlinked since the dipolar and Zeeman reservoir are coupled[179]. The effective diffusion consists of contributions from the Zeeman diffusion $D_Z$ and the dipolar diffusion $D_d$. Because of the fcc nature of the KPF$_6$ lattice structure both diffusion terms are assumed isotropic in the following analysis.

9.2 Theory

In 1975, Genack and Redfield[180] devised partial differential equations describing spin diffusion in a magnetic gradient field. The following first equation can be derived by substituting Curie’s law in their Zeeman Equation. The second equation by substituting $B = \mu_0 H$ in free space and $\nabla^2 A = \Delta A$ in the dipolar equation, see also the equations of Eberhardt et al. [179, 181]

$$\frac{\partial \beta_Z}{\partial t} = D \nabla \left( \frac{\nabla (B \beta_Z)}{B} - \frac{\nabla B}{B \beta_d} \right) - \frac{\beta_0 - \beta_Z}{T_1},$$

$$\frac{\partial \beta_d}{\partial t} = D_d \Delta \beta_d + \frac{D \nabla B}{B_d^2} \left( \nabla (B \beta_Z) - (\nabla B) \beta_d \right) - \frac{\beta_0 - \beta_d}{T_{1d}},$$

in which $\beta_Z = 1/(k_B T_Z)$ and $\beta_d = 1/(k_B T_d)$, the inverse spin temperature, where $T_1$ is the spin-lattice relaxation time, $T_{1d}$ the dipolar reservoir relaxation time and $D$ the effective diffusion constant (note that here we consider only the dipolar and Zeeman dominating interactions). Re-written in a 1-dimensional form, using $\frac{dB^2}{dz^2} = 0$

$$\frac{d}{dt} \left[ \frac{\beta_Z}{\beta_d} \right] = \left[ \frac{D}{D_d} \right] \frac{d}{dz} \left[ \frac{\beta_Z}{\beta_d} \right] + D \frac{dB}{dz} \left[ \frac{1}{B^2} \left( \frac{d^2 \beta_Z}{dz^2} - \frac{dB}{dz} \right) \right] + \frac{\beta_0 - \beta_Z}{T_1} \left( \frac{\beta_0 - \beta_d}{T_{1d}} \right).$$

A numerical evaluation of the two coupled second-order parabolic partial differential equations is obtained with Matlab. Neumann boundary conditions to the partial differential equations were applied, which means that no diffusion is assumed at the sample edges, i.e. $\partial^2 u/\partial z^2 = 0$, slab symmetry is used.

9.3 Experimental

9.3.1 Implementation

As displayed in Fig. 9.1, the experimental method of detection relies on the determination of $D$ (and $T_1$) from two MRFM data sets in a single experiment. In the first part either a full inversion
or saturation is applied as reference. When all spins within the entire volume are simultaneously saturated or inverted, the spin temperature remains constant, no net transfer of magnetization between slices takes place and the magnetization recovery in all regions will occur with approximately the same time constant. As the recovery occurs without diffusion, a simple, approximate solution is given by the well-known single exponential functions for inversion recovery respectively saturation recovery \( \beta^{IR}(t) = \beta_0 \cdot (1 - 2e^{-t/T_1}) \) and \( \beta^{SR}(t) = \beta_0 \cdot (1 - e^{-t/T_1}) \), with \( \beta_0 \) the inverse temperature at \( t = 0 \). The second pulse sequence contains a slice-selective inversion or saturation in which spin temperature levels are different per slice and diffusion does occur. As time increases the diffusion smears out an applied saturation or inversion profile. If the diffusion length is much smaller than the sample dimensions, the boundaries are not reached.

- The magnetization at \( t = 0 \) can be simulated by first convoluting the equilibrium magnetization with the excitation profile. The number of spins \( N_{\text{slice}} \) in each resonant slice depends on the shape of the sample, the slice detection width and the position of the magnetic gradient. In case of full inversion or saturation, the inverse spin temperature in the slices is homogeneously distributed and has a maximum of \( \beta_0 \) for \( t = \infty \). The slice magnetization over the sample is generally inhomogeneous, since, for the slice magnetization, the number of spins in each slice has to be considered. The number of spins is a parameter in the Curie constant \( C \) and therefore can be measured indirectly from the magnetization since \( M_i = \beta_1 \cdot B \cdot C \). Similarly to the excitation, the MRFM detection magnetization can be simulated using a convolution with the current magnetization and the Point Spread Function, PSF(\( x \))[65]. Note that in this analysis, we do not consider the three dimensional shape of the sample and the shape of the resonant slice, instead we only consider the "measured" number of spins in each slice.

- In MRFM, the slice magnetization is detected via a force on the cantilever (see Eq. 5.1). A lock-in amplifier detects this force exerted on the cantilever at its eigen frequency (see Eq. 5.39), while the spins are locked by rf waves. The MRFM intensity, displayed here in plots as a
single point for each slice, is obtained by integrating the lock-in signal during acquisition. This integrated intensity at a certain delay time, $I(t_d)$, is approximately proportional to the magnetization $M(t_d)$ (see Eq. 5.39). This time $t_d$ is the delay time as indicated in figure 9.1.

- In the MRFM experiment of Eberhardt et. al[179] multiple inversion sweeps are used during the mixing time. This is done to suppress the buildup of polarization in the dipolar bath. Here we do not suppress this buildup and determine the Zeeman and dipolar diffusion constant $D_Z$ by fitting the data.

- Versatile waveforms for saturation or inversion could be generated with a waveform generator. A band-stop/pass function is constructed using the inverse Fourier transformation of the desired band profile[65]. In this manner, it is possible to generate narrow, well-defined excitation profiles.

- We established that the drift of the gradient is less than 1.0 $\mu$m per day. The aim is to finish each diffusion experiment within one day.

9.3.2 $T_1$ relaxation times

Since the experiment is sensitive to variations in relaxation times, it is verified that a change in gradient strength from 180 T/m to 620 T/m did not systematically make $T_1$ shorter or longer, see Fig. 9.2. For these experiments the pre-heating time is set to 1.5 seconds, after which a 100 ms
saturation followed with a noise frequency band of $\pm 150$ kHz. Then the frequency is swept during 5 ms from an insweep frequency of $\pm 90$ kHz to the detection sweep width $\pm 80$ kHz. The acquisition time is 2 seconds. Because these were all saturation experiments, the repetition delay is set to only 0.2 seconds. An extra delay of 3.0 seconds had to be added due to the loading of the waveforms into the generator. The average value and standard deviation of the four experiments is $T_1 = 7.0 \pm 0.5$ s. The observed fluctuations in the $T_1$ were attributed to the relatively low SNR. The MRFM detection using spin locking requires high power during long acquisition time. This causes strong rf heating which might influence the relaxation times.

### 9.3.3 Saturation and inversion recovery experiments

Different MRFM saturation / inversion recovery experiments were done with MRFM probe design 1 (see Section 6.1). Here, we describe three specific MRFM experiments at different gradient fields. The experiments were done in a $B_0 = 4.3$ T magnet, a constantly present magnetic field gradient is generated by an iron cylinder of 300 $\mu$m diameter in close proximity to the sample. The gradient strength could be manipulated by adjusting the position of the gradient with respect to the sample. In all these experiments, the acquisition time is 3 seconds. The RF power applied to the coil is 3.0 Watt. The micro-coil had a low inductance and is not matched with a capacitor to a specific frequency. The RF power is transmitted through the coil and absorbed in a 50 Ohm load resistor ($Q = 1$).

First, a full and a slice-selective saturation recovery experiment is done at 760 T/m. A band-stop noise-function, created with a Butterworth filter of order 49 and a width of $\pm 100$ kHz around the center frequency (174.302 MHz) is designed for the slice-selective saturation. The slice-selective saturation had a duration time of 100 ms. After this, a variable delay time followed of 0.1, 1, 2, 4, 6, 8 seconds, during which constant RF power is applied at the center frequency. The RF had to remain on because of the pre-heating of the cantilever. The insweep frequency of the detection is $\pm 150$kHz and the detection width is $\pm 100$ kHz. An estimate for the number of active spins can be derived from the slice detection volume taking the PSF into account. Since the magnetic gradient is in the z-direction, the height of the slice is determined by the detection sweep width. Here, the effective slice height is $2 \cdot 150 \cdot 0.8 = 240$ kHz $\equiv 7.5$ $\mu$m. 16 Averages were acquired and 21 frequency steps were made with an interleaved step size of 4 and a step size of 50 kHz. The recycle delay is 5 seconds.

The second experiment is a full and slice-selective inversion recovery at 1270 T/m. The spatial resolution is 50 kHz/$\mu$m. An experimental grid is implemented, such that the magnetization of each interleaved slice could be either selectively inverted or not. The idea is to artificially boost the SNR by adding up slice contributions from different parts of the sample. The inversion sweep time is 5 ms. After which no power is applied for the increasing duration time intervals of 0.25, 0.5, 1, 2, 4, 8 and 16 seconds. The central frequency is 176.701 MHz. The insweep frequency of the detection is $\pm 125$kHz and the periodic detection width is $\pm 120$ kHz, thus the effective slice height is $2 \cdot 125 \cdot 0.8 = 200$ kHz $\equiv 4.0 \mu$m. 8 averages were acquired. 31 frequency steps were made with an interleaved step size of 4 and a step size of 62.5 kHz. The recycle delay is 20 seconds. The entire sequence took $\sim 17$ hours.
The final experiment is a slice-selective saturation recovery at 1550 T/m and a resolution of 64 kHz/µm. The center frequency is 177.736 MHz. A saturation grid with a 225 kHz band-pass frequency and spacing, after which power is applied for the increasing duration times of 0.001, 1, 2, 4 seconds. The insweep frequency of the detection is ±75 kHz and the periodic detection width is ±70 kHz, thus the effective slice height during detection is $2 \cdot 75 \cdot 0.8 = 120$ kHz $\equiv 1.9\mu$m. 16 Averages were acquired. The 31 frequency steps were scanned linearly, with a step size of 75 kHz. The recycle delay is set to 4 seconds.

### 9.4 Results

In the following sections, the results of the three experiments at different magnetic field gradients are discussed. First, SR at 760 T/m, then IR at 1270 T/m and finally SR at 1550 T/m. The outcome of each experiment yields a diffusion constant. The three diffusion constants will be compared in the conclusion section.

#### 9.4.1 Slice-selective/Full Saturation Recovery at 760 T/m

Figure 9.3 displays the integrated, absolute, normalized, fully saturated MRFM data. The absolute integration of the noise caused an constant offset in these graphs. This offset is determined from the data points near the edges of the sample and is subtracted. The experimental data is normalized to

![Figure 9.3](image-url)
9.4. RESULTS

Figure 9.4: The slice-selective saturation profile and the Point Spread (detection) Function. A convolution of these two yields the simulated image, labeled "sim.", the experimental data is labeled "exp."

Figure 9.5: The evolution of the slice-selective saturated data in time. Solid line is simulation including convolution with the PSF and the best fit.

the earlier determined average $T_1$ relaxation time of 7.0 seconds, the simulated lines were calculated with the same relaxation constant.

The saturation of a single slice is normalized to the intensity of the first image (at $t = 0.1\ s$). Because of the higher order terms (up to 49th order) in the waveform generation of the saturated region, the edges along either side of this selected band were very steep. The PSF is clearly responsible for the much weaker slope observed in the experimental data. Therefore, it is necessary to include the PSF in the simulation. The PSF($x$) is determined with Equation 5.36 and could be reproduced using the experimental settings $\omega_1 = 45$ kHz and $\omega_{step} = 50$ kHz $\equiv 1.56\ \mu m$. The smooth PSF reduced the capability to select a well-define narrow region with sharp edges. The differences were
mostly visible at $t \sim 0$. Figure 9.4 shows that the experimental data at $t = 0.1s$ matches with a convolution of the initial slice-selective saturation profile with the point spread function.

The slice-selective saturation experiment is shown in Figure 9.5. Fixed parameters in the simulation were $D_d = 0$ (for the moment assumed much smaller than $D_Z$), $B_0 = 4.3$T, $B_d = 20$mT, $T_1 = 7.0s$, $\gamma_F/\gamma_H = 0.94094$ and $T_{1d} = 5.9s$. As described in Section 9.2, the simulated Zeeman and dipolar diffusion is determined with numerical evaluations of equation 9.2, in which the equilibrium spin temperature is set to $\beta_0 = 1$. The initial Zeeman and dipolar polarization is given by the selective or non-selective saturation profile, see figure 9.4. The Zeeman diffusion constant $D = D_Z$ is manually determined by optimizing the overlap between experiment and simulation (see figure 9.7).

![Figure 9.6: 3D representation of the simulated $^{19}$F MRFM data at 760 T/m. (a) Zeeman diffusion. (b) Dipolar diffusion.](image)

Zeeman and dipolar diffusion spin temperature graphs are plotted in Figure 9.6a respectively 9.6b. The diffusion constant is fitted to $1.0 \pm 1.0 \text{ $\mu$m}^2/\text{s}$, this seems extremely high compared to for example CaF$_2$ (factor 6200 faster, see [179]). Unfortunately, the maximum delay after the saturation is only 8 seconds, which is insufficiently long to capture the full return of the normalized MRFM intensity to 1.0 (see figure 9.7). Therefore, the fitting of the spin diffusion constant also depends on the relative intensity of the signal in this data set.

### 9.4.2 Slice-selective and full Inversion Recovery at 1270 T/m

To determine and visualize the spin diffusion more accurately, the PSF is set more narrow and the spatial resolution is increased by increasing the gradient strength. However, both scenarios decrease the SNR. In this experiment, we furthermore used on/off switchable inversion sweeps for maximum visibility of the diffusion, thereby generating a periodically inverted grid. A simulated grid is programmed with the same initial magnetization of each slice, i.e. initial inversion sets the spin temperature to $-\beta_0$, while an unaffected slice remains at $\beta_0$. The full inversion recovery data reference set showed a good fit with a slightly lower $T_1 = 6.0$S, see Fig. 9.8. The $T_1$ might have been slightly lower due to heating, not due to a too short repetition delay. Due to compiler processing, many slices and long measurement time, the measurement time before reaching again the same slice for the next averaging step is about 600 seconds. The shortest time to reach a neighboring slice is
160 seconds. This depends on the interleave step size, however 160 seconds is sufficient, far more than $5 \times T_1$, so a full inversion for each selected slice at $t = 0$ is expected.

The data on the outer left side in the figures 9.8 and 9.9 seems saturated instead of inverted at $t = 0$. A possible explanation for this disturbance might be a low power, higher order resonance from the mixing of the RF at the start of the delay period, see [182] or disturbance in the PTS during switching of the frequency, see [183].

Figure 9.9 and 9.10 show the slice-selective inverted data, fitted with a diffusion constant of $D = 0.02 \pm 0.02 \, \mu m^2/s$. The PSF is not included here since the inversions were relatively narrow and the point to point time evolution near the slopes is a measure for the diffusion in this dataset. As an additional check, the relaxation times of the full and slice-selective inverted slices were fitted with a mono-exponential function. In this case, the average relaxation time constant of 10 slices of the full respectively slice-selective inversion times decreased from 7.6 to 6.8 seconds.
Figure 9.8: Fluor, full inversion recovery of KPF$_6$ at 1270 T/m.

Figure 9.9: Slice-selective inverted MRFM image. Markers show the experimental data, the straight lines are obtained using a numerical evaluation of the differential equations. In this data, the PSF is not taken into account.
Figure 9.10: Time view of the slice-selective inverted MRFM data. The markers show the experimental data, the three solid lines represent simulations: the blue line is simulated with a diffusion constant of 0.005 μm²/s (slower), red 0.02 μm²/s (best fit) and black 0.04 μm²/s (faster).
Figure 9.11: Fluor, spatial saturation recovery in KPF₆. Markers show experimental data, solid lines show simulated data, not convoluted with a PSF.

<table>
<thead>
<tr>
<th></th>
<th>∇B</th>
<th>spatial resolution</th>
<th>profile height during detection *</th>
<th>eff. slice height during detection</th>
<th>step size</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(T/m)</td>
<td>(kHz/µm)</td>
<td>(µm)</td>
<td>(µm)</td>
<td>(µm)</td>
<td>(µm²/s)</td>
</tr>
<tr>
<td>SR</td>
<td>760</td>
<td>32</td>
<td>6.24</td>
<td>7.5</td>
<td>1.56</td>
<td>1.0 ± 1.0</td>
</tr>
<tr>
<td>IR</td>
<td>1270</td>
<td>50</td>
<td>5.0</td>
<td>4.0</td>
<td>1.25</td>
<td>0.02 ± 0.02</td>
</tr>
<tr>
<td>SR</td>
<td>1550</td>
<td>64</td>
<td>3.56</td>
<td>1.9</td>
<td>1.19</td>
<td>0.02 ± 0.02</td>
</tr>
</tbody>
</table>

Table 9.1: Data from all spin diffusion experiments. SR = Saturation Recovery, IR = Inversion Recovery. * calculated from 2 × insweep × 0.8, converted to µm.

9.4.3 Slice-selective Saturation Recovery at 1550 T/m

The magnetic gradient is increased to 1550 T/m and the effective slice height narrowed to 1.9 µm. A slice-selective saturation recovery experiment and a single equilibrium reference image is recorded, see Fig. 9.11. From this data, the diffusion constant is estimated to be \( D = 0.02 ± 0.02 \, \mu m^2/s \). During the delay period, the off resonance frequency of the WFG is set to 2 MHz and the PTS and WFG were kept on standby. The outer right side seems to be completely saturated after 1 seconds. Again, a possible explanation for this disturbance might be a low power, higher order resonance from the mixing of the RF at the start of the delay period.

9.5 Conclusions

This feasibility study shows the capabilities of MRFM setup design I for the detection of spin diffusion in materials with a relatively short \( T_1 (\sim 10 \, s) \). A summary of the experiments at the
three different gradient strengths is given in table 9.1. The value for the diffusion constant could not be reproduced and varied from 0.005 to 2.0 \( \mu \text{m}^2/\text{s} \) for the different experiments at different magnetic field gradients. The trend seems to be that the diffusion constant decreases at stronger magnetic field gradient. However, the diffusion constant should not be dependent on the gradient field strength itself. Furthermore, it is highly unlikely that the spin diffusion constant varies much with the orientation of the crystal (a different experiment means a different orientation on the cantilever), since the crystal lattice is fcc, with a relatively high radial symmetry. The spin diffusion constant could be temperature dependent due to the rotation of the PF\(_6\) group, but the diffusion constant is not expected to be 50\( \times \) higher for an experiment at 760 T/m with respect to 1270/1550 T/m. We therefore conclude that the experiment at 760 T/m most likely varied in relative intensity and that the reproducibility, stability and gradient strength of this setup seems insufficient to reliably determine the diffusion constant of KPF\(_6\).

### 9.6 Outlook

What is required to be able to visualize the spin diffusion in KPF\(_6\)? If we assume a similar Zeeman diffusion constant as CaF\(_2\), \( i.e. \) 0.0006 \( \mu \text{m}^2/\text{s} \), the displacement should be detectable within the much shorter relaxation time of about 10 seconds. The \( \sqrt{2}DT_1 \sim 100 \) nm displacement should be detected with a SNR of at least 5. If we reduce the distance to the gradient to 100 \( \mu \text{m} \), this results in a gradient field of 3.2 kT/m and a resolution of 140 kHz/\( \mu \text{m} \). To detect a 0.1 \( \mu \text{m} \) thin slice in a 10x10x10 \( \mu \text{m} \) sample, the sweep amplitude is 15 kHz and the detectable force 14 fN (\( k_c = 0.01 \) N/m). At room temperature 40,000 acquisitions are needed to get a SNR of 5, at 77K 3,000 averages and only 2 averages are needed at 2 K, although relaxation times may be different. The stability/reproducibility/drift needs to be better than 50 nm during the possibly rather lengthy measurement time.
Appendices
Appendix A

MRFM hardware overview

PC Including a National Instruments Analog Waveform Generator (AWG) card DAQ Arb5411, a National Instruments multi-purpose I0card PCI-MIO-16e-1, with two internal counters, two analog in- and outputs and 8 digital outputs and a GPIB card for communication with the lock-in amplifier. Digital output A digital output from the I0card was used for the blanking of the amplifier. Lock-in amplifier Stanford Instruments SR830 including GPIB interface to PC. Optimal control feedback The analog input is received via the external reference channel, the analog output waveform to the cantilever piezo can be set in the software. RF analog multiplier The ‘SpinBrush’ multiplies the AWG frequency (typically around 10..14 MHz) with the PTS frequency (10..200 MHz). PTS 200 digital synthesizer Switchable for 2 channel operation, set via the parallel out, printer port of the PC. Low frequency filtering To reduce noise, mainly below 50 Hz, from the interferometer. RF power amplifier The BLAX 5 (5 Watt) or the BLAX 1000 (300W output channel) Laser Toshiba TOLD 9215 laser diode Single mode fiber optics Gould Nufern 630HP fiber with a 2x2 50/50 bi-directional coupler, an APC/APC connector from Compose and 2 x Thorlabs custom single mode 670nm fiber for attachment to the two probes. Photo-diodes Thorlabs IO-3D-670-VLP with a selectable range of 0..70dB amplification. Subtraction electronics Opamp, for R-n-F, n=0...1 the setting of the potentiometer. XYZ piezo power amplifier Design I, controlled via the lock-in auxiliary output. Atto-cubes Design II, two ANPx50 and the ANPz50 and a controller. The communication with the controller occurred via RS-232 over the PC port COM2.
Appendix B

Labview control of the PC hardware

To control these hardware devices, Labview 8.2 facilitates the use of global virtual channels. For synchronization and timing of the pulse sequences with the hardware, we can use the internal Real-Time System Integration (RTSI) bus (see table B.1).

<table>
<thead>
<tr>
<th>Analog input channel</th>
<th>connected to</th>
<th>global virtual channel name</th>
</tr>
</thead>
<tbody>
<tr>
<td>dev1/a0</td>
<td>Fiber Interferometer Forward</td>
<td>FiberInterferometer In</td>
</tr>
<tr>
<td>dev1/ai1</td>
<td>Fiber Interferometer Reflected</td>
<td>FiberInterferometerDirect In</td>
</tr>
<tr>
<td>ext. ref.</td>
<td>Test signal, optimal control out</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Analog output channel</th>
<th>connected to</th>
<th>global virtual channel name</th>
</tr>
</thead>
<tbody>
<tr>
<td>dev1/ao0</td>
<td></td>
<td>Cantilever Piezo Out</td>
</tr>
<tr>
<td>dev1/ao1</td>
<td></td>
<td>Fiber Piezo Out</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Internal wire connections</th>
<th>connected to</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>RTSI 5</td>
<td>Start Acquisition (marker)</td>
<td></td>
</tr>
<tr>
<td>RTSI 4</td>
<td>Start WFG</td>
<td></td>
</tr>
<tr>
<td>20MHz time based counter</td>
<td>RTSI 7 / clock -&gt; WFG clock</td>
<td></td>
</tr>
</tbody>
</table>

**Table B.1:** Global virtual channels and RTSI routing
Appendix C

Cantilever and sample mounting procedure

1. (MRFM design I) Mount the cantilever and fix its clamping spring.

2. (MRFM design I) Align the legs of the cantilever stage with the stereo microscope. With decreasing magnification, the reflection of the chip has to be kept optimal, while the stage is rotated over 360 degrees.

3. Search a sample of correct size, aim for a cantilever frequency around 1 kHz. Depending on the density of mass of the sample and the spring constant of the cantilever, this determines the sample dimensions. The dimensions of the sample can be estimated using the optical grid in the microscope ocular.

4. Mix the two component glue for 1 minute, until it becomes non-transparent / slightly white.

5. Put the glue on the tip of the arm with the biggest tip and mount the arm into the micromanipulator. Use it to put the glue on the cantilever.

6. Pick up the sample with the sharp 140 degree arm, by static forces and fix it onto the cantilever.

7. Put a lamp or heater near the sample for a minimum of 15 minutes, until the glue is hardened.

8. Check resonance frequency in the MRFM setup.

9. (MRFM design I) Fix the coil.

In design II, the cantilever is glued up-side down into its mount and the sample is fixed onto the back of the cantilever. The The Atto-cube alignment is fixed to the probe. A good optical alignment can be verified using inline optical reflection of the cantilever surface and the fiber end. Another option is to use the Labview program 'Fiber Align’. It monitors the reflectivity, contrast and sensitivity.
Appendix D

Hardware connections overview

Figure D.1: Overview of the hardware connections.
Appendix E

Software overview

**Figure E.1:** Overview of the software functionality.
Appendix F

Timing and synchronization

Figure F.1: Overview of the MRFM timing and synchronization.

A National Instrument PCI-MIO-16E-1 IO card controlled the blanking and timing of the RF, using the two internal hardware counters. One counter was used to generate the frequency of the cantilever, while the other was used for the timing of the (optional) switching between two programmable RF frequencies. The Programmable Test Sources, Inc. (PTS) 250 was equipped with latches for storage of two separate frequencies. The parallel port of the PC was used to set the latches in advance to the correct decimal values for the two frequencies. The waveform generator
board was a 40 MHz, National Instruments (NI) 5411.
Appendix G

Available waveform instructions

The available waveform instructions:

- AdrfDown/Up - ADRF/ARRF. Ramps the amplitude linearly.
- AdrfDown/UpNew - ADRF/ARRF. Ramps the amplitude with constant adiabaticity.
- BandPassNoiseFFT - Saturates a frequency band.
- Carrier - Create a waveform of carrier frequency.
- CarrierInterleave - Create a wave at an interleave frequency.
- Center - Set the center frequency.
- CenterInterleave - Set the center interleave frequency.
- CompensateTiming - A delay used to synchronize time variable sequences.
- DetectFunc - Detection waveform.
- DFSweep - Double frequency sweep.
- FixedSech - Fixed frequency secant hyperbolic, use with quadruplexer only.
- FixedSweep - Fixed frequency sweep.
- HahnEcho - \( \frac{\pi}{2} - t_1 - \pi - t_2 - \frac{\pi}{2} \)
- Init - Initialize the AWG sequentially.
- LongDelay - Delay longer than 1 ms.
- NewPulsePhase - Single pulse.
- Run - Starts the pulse program.
- Sech - Secant hyperbolic.
- SelectSweep - If grid function returns true, execute sweep.
- SetAcqPhaseLockin - Set the detection acquisition phase.
- SetPhaseRF - Set the current RF phase.
- ShortDelay - Delay shorter than 1 ms.
- Sweep - Generate single sweep.
Appendix H

Example pulse program, Hahn-Echo

extern vH=182.6e6
extern ratio=0.94094011
extern acqtm=2
extern pd=25
extern pw90a=5e-6
extern pw180=10e-6
extern pw90b=5e-6
extern t1=0:4e-6:40e-6
extern navg=1:8
extern hif ampl=80e3
extern offres=1e6
extern aX=0.7
extern pamp=1
extern pretime=1
extern WFG=14e6
begin {
  LOOP2D (t1) {
    LOOP1D (navg) {
      Init(WFG)
      Center(vH*ratio,0)
      STAGE (1)
      SetAcqPhaseLockin(0)
      CompensateTiming(t1)
      Carrier(aX,pretime,offres,1000)
      SetPhaseRF(0)
      HahnEcho(pamp,t1/2,t1/2,pw90a,pw180,pw90b,180,270,0)
      DetectFunc(aX,acqtm,0,hif ampl,0,0)
      Run(navg,pd)
    }
    STAGE (2)
    SetAcqPhaseLockin(0)
    CompensateTiming(t1)
    Carrier(aX,pretime,offres,1000)
    SetPhaseRF(0)
    HahnEcho(pamp,t1/2,t1/2,pw90a,pw180,pw90b,180,270,0)
    DetectFunc(aX,acqtm,0,hif ampl,0,0)
Run(navg, pd)
}
}
}
Appendix 1

Setting up an MRFM measurement

The software of the spectrometer was developed under Labview 8.2, with operating system Microsoft XP. To start an MRFM measurement, we first calibrate our cantilever system.

1. By starting the 'cantilever control.vi' the following panel will appear (see Figure I.1). The interferometer response is directly displayed in the voltage graph. By clicking on 'Fiber Align', a triangular wave function is sent periodically, with delays, to the fiber piezo (put the z-channel switch of the Attocube console to external). The contrast and sensitivity is displayed for each iteration and the position of the cantilever and fiber can be optimized, while monitoring the response. When the alignment is done, a sinus pattern will appear in the interferometer response graph. The vertical lines can be set to restrict the range of the fiber piezo. The sensitivity is written in the parameter panel (see Figure I.2). By use of the tabs, within this panel, it is possible to estimate the mass, the Larmor frequency, the spatial image resolution, the B1 field and the SNR ratio. The set-point is always fixed to 0 Volt and should be matched as best as possible with the potentiometer.

2. Measure the cantilever resonance spectrum and verify that the calculated spring constant is within 10% of the theoretical value. The cantilever resonance frequency should be around 1 kHz.

3. Switch the vacuum on. Wait until the pressure drops below $10^{-4}$ mbar.

4. Run the 'get f and Q' function from the cantilever control panel. Change the flank of the feedback and verify that the Q factor is not affected too much, otherwise too much laser power is used. Set the laser power around at its optimal value, typically 50 $\mu$W.

5. Fill in the detection limit, which can be obtained from the cantilever resonance spectrum and the Q desired. Start the optimal control, adjust the amplitude, so that the motion is restricted to one fringe. Manually adjust the hardware knobs of the optimal control to the
values mentioned in the parameter panel. The cantilever can start to oscillate, this could mean that the current fringe position has the opposite flank. By moving the vertical lines on the user interface of the cantilever control, the fringe position can move to its correct fringe for proper functionality of the optimal control.

6. (Optional) Run the 'wait for hardware trigger' and verify that the triggering is working correctly.

7. Start the acquisition panel (see figure I.3) and select the working path of the sequences and select the program.

8. Verify that the RF output power is correct and does not change much over the frequency range.

9. In the process panel (see figure I.4), all data can be recalled and analyzed.
Figure I.2: MRFM parameter panel.
Figure I.3: Acquisition panel.
Figure I.4: Processing of the MRFM results.
Appendix  J

MRFM practical improvements

HARDWARE

• In MRFM probe design I there was a strong drift of the position of the fiber. In some cases, this would mean that over time the optical sensitivity would decrease. This was mainly caused by μm creep in the x-y positioner, which used an elastic material that aged and became brittle within a period of two years. It was possible to fix the positioner from two sides, tightening the positioner to reduce the creep.

• In MRFM probe design I there was a drift of the gradient was visible in the frequency (~ 1 μm/day)

• There could be an increase of $T_1$ and decrease of $T_{1\rho}$ after time, due to temperature increase, because of the constant application of RF power. It is preferred not to use too high powers (know what you are doing above 3 Watt).

• The PC should be upgraded or the loading of the sequence into the WFG should be implemented differently. The loading times were ~3 seconds, every time a stage list of .vi files is loaded into the WFG.

• A proper optical table should be used, often the optical table had 'flat tires'.

• A trigger card should be installed for easier timing. At this moment the timing is limited by using the two internal counters. The accuracy is determined by the frequency resolution of the IO card.

SOFTWARE

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• The MRFM phase should be consistent for each scan. In a time-dependent experiment, this was solved by adding a time compensation delay in front. It is better to start acquisition on the detect sequence, not via a counter. To implement this, an additional counter or a trigger card is needed.

• Synchronize on the AWG without using counter1.

• Implementation of a proper triangular sweep function.

• Build in the possibility for handling more phase-cycling in the compiler.

• The compiler should output a warning in case there are unused variables in the pulse sequence input file. Small typos can then be circumvented.
Appendix K

Simpson scripts

K.1 Hahn-echo

spinsys {
    channels 76As
    nuclei 76As
    quadrupole 1 2 1e6 0.1 0 0 0
}

par {
    proton_frequency 800e6
    sw 5000000.0
    np 4000
    ni 1
    crystal_file $crystal_file
    gamma_angles 1
    start_operator 11z
    detect_operator 11p
    verbose 1111
    variable dw 1000000.0/sw
    variable t_acq np*dw
    variable tau1 200 #al3ga7, 175us for al5ga5
    variable tau2 100 #al3ga7, 15us for al5ga5
    variable rf 625000
    variable t90 0.125e6/1f #sel. pulse I=5/2 (75As) 0.2us exp.
    variable t180 0.25e6/1f #0.4us exp.
}

proc pulseq {} {
    global par
    #prop 1 - for acq
    reset
delay $par(dw)
store 1

    #actual pulse program
reset

221
pulse $\text{par}(t90) \ \text{par}(rf) \ [\text{linx} \ \{x -x\} \ \text{par}(p)]
\text{delay} \ \text{par}(tau1)
pulse $\text{par}(t180) \ \text{par}(rf) \ [\text{linx} \ \{-y \ -y\} \ \text{par}(p)]
\text{delay} \ \text{par}(tau2)
\text{acq} \ \text{par(np)} \ 1 \ [\text{linx} \ \{x -x\} \ \text{par}(p)]
\}

proc main () {
\global \text{par}
\foreach \text{site} \ 0 \ 1 \ 2 \ {
\if \{$\text{site}==0\}$ \ {
\\# central + satellites
\\for \{\text{set par}(etaT) 0\} \ {\$\text{par}(etaT)<=100\} \ {\text{incr par}(etaT) 5\} \ {\{
\\\\text{for} \ \{\text{set par}(Qcc) 0\} \ {\$\text{par}(Qcc)<=1400000\} \ {\text{incr par}(Qcc) 200000\} \ {\{
\\\\text{set par}(eta) \ [\text{expr} \ \text{par}(etaT)/100.0]$
\\\\text{set par(name) A}
\\\text{set par(crysatl_file) zcv4180}
\\\text{set par(detect_operator) I1p}
\\text{run}
\\}
\}
\}\}
\}
\}
\if \{$\text{site}==1\}$ \ {
\\# central transition
\\for \{\text{set par}(etaT) 0\} \ {\$\text{par}(etaT)<=10\} \ {\text{incr par}(etaT) 1\} \ {\{
\\\\text{for} \ \{\text{set par}(Qcc) 3100000\} \ {\$\text{par}(Qcc)<=35000000\} \ {\text{incr par}(Qcc) 100000\} \ {\{
\\\\text{set par}(eta) \ [\text{expr} \ \text{par}(etaT)/100.0]$
\\\\text{set par(name) B}
\\text{set par(crysatl_file) zcv28666}
\\text{set par(detect_operator) I1c}
\\text{run}
\\}
\}
\}
\}
\if \{$\text{site}==2\}$ \ {
\\# central transition, eta 1 is assymetirc -> more orientations needed!!
\\for \{\text{set par}(etaT) 92\} \ {\$\text{par}(etaT)<=100\} \ {\text{incr par}(etaT) 1\} \ {\{
\\\\text{for} \ \{\text{set par}(Qcc) 3100000\} \ {\$\text{par}(Qcc)<=35000000\} \ {\text{incr par}(Qcc) 100000\} \ {\{
\\\\text{set par}(eta) \ [\text{expr} \ \text{par}(etaT)/100.0]$
\\\\text{set par(name) C}
\\text{set par(crysatl_file) zcv28666}
\\text{set par(detect_operator) I1c}
\\text{run}
\\}
\}
\}
\}
}
\}

proc run () {
\global \text{par}
\text{set interactions [list \ \"quadrupole_i_aniso $\text{par}(Qcc)\" \ \"quadrupole_i_eta $\text{par}(eta)\""]
\# 2step phase-cycling
\for \{\text{set par}(p) 0\} \ {$\text{par}(p)<2\} \ {\text{incr par}(p)\} \ {\{
\\text{set} \ z \ [\text{fsimpson} \ \text{interactions]}
\}
if [info exist g] {
    fadd $g $f
} else {
    set g [dup $f]
} funload $f
}

if {$par(name) == "A"} {
    set naam [format "%s-%i.2f-%010.1f.fid" A [expr $par(eta)] [expr $par(Qcc)]]
    fsave $g $naam
}
if {$par(name) == "B"} {
    set naam [format "%s-%i.2f-%010.1f.fid" B [expr $par(eta)] [expr $par(Qcc)]]
    fsave $g $naam
}
if {$par(name) == "C"} {
    set naam [format "%s-%i.2f-%010.1f.fid" C [expr $par(eta)] [expr $par(Qcc)]]
    fsave $g $naam
}
funload $g

K.2 QCPMG script

spinsys {
    channels 75As
    nuclei 75As
    quadrupole 1 2 1e6 0.1 0 0 0
}

par {
    proton_frequency 800e6
    sw 4000000.0
    np 500
    ni 1
    crystal_file $crystal_file
    gamma_angles 1
    start_operator 1lx
    detect_operator 1lp
    verbose 1111
    variable dw 1000000.0/sw
    variable t_acq np*dw
    variable t_halfacq t_acq/2.0
}

proc pulseq {} {
    global par
    reset
    delay $par(dw)
    store 1

    reset
    acq $par(np) 1 x
}

proc main {} {
global par
foreach site {0 1 2} {
    if {$site==0} {
        for {set par(eta) 0} {$par(eta)<=100} {incr par(eta) 10} {
            for {set par(Qcc) 0} {$par(Qcc)<=2000000} {incr par(Qcc) 200000} {
                set par(e)/a [expr $par(eta)/100.0]
                set par(name) A
                set par(crystal_file) zcw4180
                run
            }
        }
    }
    if {$site==1} {
        for {set par(eta) 0} {$par(eta)<=10} {incr par(eta) 10} {
            for {set par(Qcc) 31000000} {$par(Qcc)<=35000000} {incr par(Qcc) 100000} {
                set par(e)/a [expr $par(eta)/100.0]
                set par(name) B
                set par(crystal_file) zcw28656
                run
            }
        }
    }
    if {$site==2} {
        for {set par(eta) 90} {$par(eta)<=100} {incr par(eta) 1} {
            for {set par(Qcc) 31000000} {$par(Qcc)<=35000000} {incr par(Qcc) 100000} {
                set par(e)/a [expr $par(eta)/100.0]
                set par(name) C
                set par(crystal_file) zcw28656
                run
            }
        }
    }
}

proc run {} {
    global par
    set interactions [list "quadrupole_1_aniso $par(Qcc)" "quadrupole_1_eta $par(eta)"
    set f [f simples $interactions]
    if {$par(name) == "A"} {
        set naam [format "%s-%.2f-%010.1f.fid" A [expr $par(eta)] [expr $par(Qcc)]]
        fsave $f $naam
    }
    if {$par(name) == "B"} {
        set naam [format "%s-%.2f-%010.1f.fid" B [expr $par(eta)] [expr $par(Qcc)]]
        fsave $f $naam
    }
    if {$par(name) == "C"} {
        set naam [format "%s-%.2f-%010.1f.fid" C [expr $par(eta)] [expr $par(Qcc)]]
        fsave $f $naam
    }
    funload $f
}
Bibliography


[7] *LiNbO₃ experiment*. Experimentally, it was observed that the piezo-electric effect of LiNbO₃ distorted the Niobium NMR signal. Therefore, a Hahn-echo sequence was employed. The resonance frequency was 146.668120 MHz, the fitted spectrum had 2.7 kHz Gaussian broadening. Experimentally, we obtained $C_q = 23 \pm 0.5$ MHz, $\delta_{iso} = -987 \pm 10$ ppm referenced to KNbCl₆. Prasad *et al.* [184] find with MAS and 3QMAS that $\delta_{iso} = -1004 \pm 5$ ppm relative to NbCl₅ and the quadrupolar constant $C_q = 22.1 \pm 0.5$ MHz with axial symmetry $\eta = 0$.


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[21] P. Kniitn. The energy levels of an atom have a fine structure due to the coupling of the electron orbital angular momentum to the electron spin. Closer observation of the energy levels reveals a hyperfine structure which is due to the participation of the proton spin. The hyperfine coupling or J-coupling results from the interactions of the nucleus with internally generated electric and magnetic fields. The hyperfine coupling is a result from the interaction between the magnetic moments associated with electron spin and the electrons’ orbital angular momentum.


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during growth of In0.5Ga0.5P GaAs heterostructures by gas source molecular beam epitaxy using


[99] J. E. Bernard, S. Froyen, and A Zunger. Spontaneous surface-induced long-range order in


Ordering dependence of carrier lifetimes and ordered states of Ga0.52In0.48P GaAs with degree

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[103] M. Goswami, P. J. Knijn, G. J. Bauhuis, J. W. G. Janssen, P. J. M. van Bentum, G. A. de Wijs,
and A. P. M Kentgens. Stripline 75as nmr study of epitaxial semiconductor al0.5ga0.5as. *J.


[114] P. Knijn. - The second moment was calculated from atoms up to the sixth shell, assuming a simplified 50 percent ¹¹⁵In, percent ⁶⁰Ga and 20 percent ⁷¹Ga occupation in the second, fourth and sixth shell. The strongest contribution (~60 percent) was from the 12 Indium/Gallium atoms in the second shell at 4 Å.


[143] J. Marohn. - Looking at the data from the interferometer, the signal with noise is incoherent, but the auto-correlation is coherent. Contribution from the talk of John Marohn - MRFM Summerschool 2004 - Kavli Institute - Cornell University - USA.


[145] - In case of Gaussian noise the equivalent noise bandwidth of the lockin amplifier can be calculated with $b_w = 1/(4\tau_L)$, for an effective filter slope of 6dB/octave, $1/(8\tau_L)$ for 12dB/oct., $3/(32\tau_L)$ for 18dB/oct. and $5/64\tau_L$ for 24dB/oct. Typically the filter slope was set to 6dB/oct.

[146] - The difference with the SNR equation in the thesis of C. Degen[65] is that the $h^2$ is now correctly replaced with $h^2$, the $T_{1p}$ is replaced by $T_{1m}$. The molecular nuclear fraction $V_{frac}$ in considered in $\rho_{spin}$.


[149] - The absolute sign is placed because of the imaginary values. The number of points that are acquired with the sample rate should be divided out in $U_{int}$. Obviously, the full signal should be acquired, otherwise $U_{int}$ will have a decreased intensity. To determine the force, we have filled in $Q = Q_{open}$ in this Eq. Experimentally, the lock-in detection voltage $U(t)$ can
directly related to the resonant displacement \( y \) of the cantilever via \( U(t) = y(t) \cdot S \), with \( S \) the sensitivity in V/m. The lock-in amplification factor is omitted for clarity.


[160] P. Knijn. -. The sapphire ball lens with 500 \( \mu \)m diameter was supplied by Edmund Optics, stock number NT46-117.

[161] P. Knijn. -. A supplier of such a lens with a relatively short working distance was Brimrose. The housing material was brass. The lens was attached to a Corning fiber with a 0.9 mm jacket via FC/APC connector. FOC-670-S-001-60-3A-9-01-5.

[162] P. Knijn. -. A spectrum analyzer was used to analyze the different laser spectra. The spectrum analyzer was first calibrated with an external source and a volt meter. The measurements were done via the lock-in amplifier and the filter/buffers. The lock-in amplifier could amplify the low voltages to 0...10 Volt, using the full dynamic range of the ADCs of the PC. The Analog to Digital Converter (ADC) of the PC was set to 250 kS/s and 250k frames. The lock-in amplifier was fixed to 1 Volt range and 6 dB/oct filter slope giving a fixed lock-in amplification.

[164] P. Knijn. - The minimum detectable force can be calculated in three ways. First with Eq. 5.22, substituting $Q_{open}$ gives 2.3 N. Second, from the fitted cantilever spectrum we obtain $S_u$ values for the open loop $S_u = 10^5$ pm$^2$/Hz and $F_{min} = 2.2$ N. Finally, from the fitted closed optimal control loop ($Q_{closed} = 20$) cantilever spectrum we obtain $S_u$ values for the closed loop $S_u = 40$ pm$^2$/Hz and $F_{min} = 2.2$ N. By comparing the last two results, it was verified that the optimal control functions properly.


[171] P. Knijn. - The $T_1$’s were determined with saturation recovery. Lin et al. [17] mention a lower $T_1/\rho^P$, but otherwise similar values at 5.6 Tesla and similar $B_1$ fields.


[181] P. Knijn. * K. Eberhardt et al. wrongfully mentions a second D in the upper equation (to match our equation, which has also correct units, their second D is set to 1). Furthermore $\nabla(B\beta) = B\nabla(\beta) + \beta\nabla(B)$ was misinterpreted by K. Eberhardt et al. and is used here correctly, resulting in a different expression for the 1-D matrix Equation. Note that their paper does not mention the 1D equation.

[182] P. Knijn. * Higher order resonances were observed on the spectrum analyzer. The main RF power was observed at the desired frequency and about the same power at + or - the 14 MHz WFG center carrier frequency. Higher order mixing terms were also observed and a wide band width filter could reduce the output power in these unwanted higher order frequencies. During delay time, the PTS was kept at constant power, but the WFG frequency was set to 4 MHz off-resonance (outside of spectral range) with 0 power. Because of the larger RF spacing (in MHz) this seems unlikely, on the other hand, only low power during a short time (glitch) of a non-linear term would have been enough to saturate the magnetization at this specific frequency.

[183] P. Knijn. * Before the delay time the PTS frequency was switched, while the power of the PTS channel was kept on, this could also explain the disturbance, specifically around t=0. Note however that the reference set did not show this saturation and was generated in a similar manner.

Summary

In order to understand the properties of III/V semiconductors, knowledge about their ordering and spatial atomic structure are of crucial importance. Nuclear Magnetic Resonance (NMR) is a versatile technique which can be used to conduct such research. The first part of this thesis describes the research about two thin film III/V semiconductors AlGaAs and InGaP with NMR.

In the first part different NMR experiments are conducted, such as QCPMG, Hahn-echoes, nutation and MQMAS of the quadrupolar nuclei Al, Ga and As. The first study was done with the thin film AlGaAs crushed to a powder and a micro-coil was used as excitation and detection resonator. A second study was done with the thin film mounted on top of a strip-line. The research consisted out of an evolutionary algorithm to fit the $^{75}$As spectra, a superpositions model which uses a single DFT simulation to calculate EFG distributions and a modified theoretical 'Extended' Gaussian Isotropic Model of Le Caër and Brand. In both studies there were no indications for long distance cation order. In the strip-line study the five $^{75}$As resonances were better spectrally resolved. Because of this, it turned out that for the Al$_2$Ga$_2$As surrounding of Arsenic there was a wider quadrupolar distribution. This can be explained by small local positional variations in the first coordination shell due to different surroundings disturbing the perfect tetrahedral symmetry of each Arsenic site.

In the next chapter a $^{31}$P NMR analysis of InGaP determines the long-range CuPt cation ordering for two InGaP samples, grown at different pressures. The bandgap energies of the two samples was measured and with these energy values a slightly higher CuPt order parameter of 0.22 at 20 mbar respectively 0.39 at 50 mbar was derived. The measured NMR relative intensities of the five $^{31}$P surroundings were in agreement with these long range CuPt order parameter values. Furthermore, the $^{115}$In and $^{71}$Ga MQMAS spectra did not reveal clear distinctions between the two samples. A clear difference with the structure of AlGaAs is the stress in the InGaP lattice. This is because difference in the lattice constants between InP and GaP is not so small as between AlAs and GaAs. It is therefore important to do structural relaxation with respect to the ideal zincblende postions to obtain a better match with the experimental results.

In the second part, the results from the research with mechanically detected NMR are presented. The MRFM part contains theory, design and applications of Magnetic Resonance Force Microscopy. Something that the NMR community has been troubled with for years, is the intrinsic low sensitivity of NMR. Because of low availability of material, a limited actively resonant volume, a low
gyromagnetic ration and/or broad resonances in the spectra, a low SNR is often a bottle-neck in many NMR experiments. It is clear that the technique of MRFM can significantly enhance the SNR in comparison to conventional inductive detection.

A novel MRFM probe was designed and diverse technical aspect of the prototype were tested. The magnetic gradient with a relatively large ferromagnetic volume had a strong electro-static interaction with the cantilever on micro-meter distances. NMR nutation data of a new designed strip line showed an relatively inhomogeneous RF field, but the maximum strength was about 130kHz at only 1 Watt power. In collaboration with the ETH Zurich we showed that it was possible to measure all nuclei in an AlGaAs thin film with an extremely small volume of 10x10x1.0 μm. The transfer of polarization from phosphorus to fluor in KPF₆ with ADRF was shown with MRFM. Finally, the effect of nuclear spin diffusion on the magnetization of Fluor in KPF₆ was extensively studied experimentally and theoretically. The results give a good indication of the possibilities and limitations of MRFM in this setting.
Samenvatting

Voor het begrijpen van de eigenschappen van III/V half-geleiders is kennis van de ordering en ruimtelijke atoom structuur van cruciaal belang. Kern spin magnetische resonantie (NMR) is een veelzijdige techniek waarmede zo’n structuur onderzoek kan worden gedaan. Het eerste deel van deze dissertatie beschrijft het onderzoek van twee dunne film III/V half-geleiders AlGaAs en InGaP met behulp van NMR.

In het eerste deel zijn verschillende NMR experimenten uitgevoerd zoals QCPMG, Hahn-echoes, nutatie en MQMAS van de quadrupole kernen Al, Ga and As. De eerste studie was met een dunne film AlGaAs vergrijsd tot poeder vorm en met een micro-spoel als excitatie en detectie resonator. Een tweede studie was met de dunne film gemonteerd op een zogenaamde 'strip line'. Het onderzoek bestond uit een evolutionair algoritme voor het fitten van de $^{75}$As spectra, een superpositie model om m.b.v. een enkele DFT simulatie, de EFG distributies te berekenen en een aangepast theoretisch 'Extended' Gaussian Isotropic Model van Le Caër en Brand. In beide studies zijn geen aanwijzingen gevonden voor lange afstand kation orde. In de strip line studie waren de $^{75}$As resonanties beter spectraal oplosbaar, waaruit bleek dat voor de Al$_2$Ga$_2$As omringing van Arseen de quadrupole distributie toch breder was. Dit kan verklaard worden door kleine lokale positie variaties in de eerste coordinate schil door de verschillende omgevingen, die de perfecte tetraheider symmetry gezien vanuit elk Arseen atoom verstoren.

In het volgende hoofdstuk wordt in een $^{31}$P NMR analyse van InGaP de lange-afstand CuPt kation orde bepaald voor twee InGaP wafers die bij verschillende druk gegroeid waren. De bandgap energie voor de twee samples was gemeten en wanneer deze wordt omgerekend naar een orde parameter blijkt dat de InGaP wafers een relatief lage CuPt orde parameter hebben van 0.22 bij 20 mbar, respectievelijk 0.39 by 50 mbar. De gemeten NMR relative intensiteiten van de vijf $^{31}$P omringingen komen overeen met de orde parameter waarden. Daarnaast waren er in de $^{115}$In en $^{71}$Ga MQMAS spectra van de twee samples geen sterke verschillen te zien. Een duidelijk verschil met de structuur van AlGaAs is de stress in het InGaP rooster. Dit komt doordat de rooster constanten voor InP en GaP liggen niet zo dicht bij elkaar als AlAs en GaAs. Het is daarom van belang om structuur relaxatie te doen ten opzicht van de ideal zinclende posities voor een betere match met de experimentele resultaten.

In het tweede deel worden de resultaten van het onderzoek met mechanisch gedetecteerde kern spin magnetische resonantie (MRFM) gepresenteerd. Het MRFM gedeelte bevat theorie, ontwerp
en toepassing van mechanisch gedetecteerde kern spin magnetische resonantie. Iets waar de NMR gemeenschap al jaren last van heeft is de intrinsieke lage gevoeligheid van NMR. Vanwege weinig materiaal, een beperkt actief meet volume, een lage gyro-magnetische ratio en/of breede resonanties in het spectra is een te lage SNR vaak een bottle-neck voor veel NMR experimenten. Het is duidelijk dat de techniek van mechanische detectie het signaal-ruis niveau aanzienlijk kan verbeteren ten opzichte van conventionele inductieve detectie.

Een nieuwe MRFM probe was ontworpen en diverse technische aspecten van het prototype zijn getest. De magnetische gradient in het orginele ontwerp, met een relatief groot ferro-magnetisch volume, had op micro-meter afstand een sterke electro-statische interactie met de cantilever. NMR nutatie data van een nieuw ontworpen stripline liet een relatief inhomogene RF veld sterkte zien, maar wel met een sterkte van 130kHz bij slechts 1 Watt vermogen. In samenwerking met ETH Zurich was aangetoond dat het met MRFM mogelijk is om alle kernen in een dunne film AlGaAs te meten met een zeer klein volume van 10x10x1.0 μm. De polarisatie overdracht van Fosfor naar Fluor in KPF₆ met behulp van ADRF is aangetoond met MRFM. Ten slotte is er een uitgebreide experimentele en theoretische studie gedaan naar het effect van kern spin diffusie op de magnetisatie voor Fluor in KPF₆. De resultaten geven een goede indicatie van de mogelijkheden en beperkingen van MRFM in deze setting.
List of Publications

Master  Multimode fiber matched Arrayed Waveguides Grating -based (de)multiplexer for short distance communications, S. Musa, A. Borreman, G. Pandrau, P. Knijn, G. Sengo, M.B.J. Diemeer and A. Driessen


Ph.D.  A Stripline $^{75}$As NMR Study of Epitaxial III-V Semiconductor $Al_{0.5}Ga_{0.5}As$, M. Goswami, P. J. Knijn, G.J. Bauluis, J.W.G. Janssen, P. J. M. van Bentum, G. A. de Wijs, A. P. M Kentgens

Ph.D.  A Multi-Nuclear Magnetic Resonance And Density Functional Theory Investigation of the Epitaxially Grown InGaP$_2$, P.J. Knijn, P.J.M. van Bentum, C.M. Fang, G.J. Bauluis, G.A. de Wijs and A.P.M. Kentgens
to be published Phys. Chem. Chem. Phys.
Curriculum Vitae

1976  Born Obdam, The Netherlands
1988 - 1994  HAVO, Han Fortmann College, Heerhugowaard
1994 - 1995  Propeadeuse HTS Electronics, Hogeschool Alkmaar
1995 - 2001  Student Applied Physics, Technical University of Twente, Enschede
2000 - 2000  Internship at Corus IJmuiden. Design of a new prototype magnetic scanner for the detection of non-magnetic particles. This research also led to the development of a new sensor concept to scan tube welds.
2000 - 2001  Master project Light-wave Devices Group of the Mesa+ research center of the Technical University of Twente. Simulate, design, fabricate and characterize an arrayed waveguide grating for wavelength (de)-multiplexing. Novel design of a multi-mode fiber matched broadband arrayed waveguide grating.
2002 - 2004  Optical engineer, Research, consultancy, development and fabrication of advanced metrology systems, such as opto-electronic (inspection) systems, measuring devices and sensors.
2009 - 2010  Physics Development Engineer ASML / TMC, Simulate, design, test and integrate the reticle stage tilt calibration test software for the extreme UV scanners
2010 - 2012  Physics Development Engineer ASML / TMC, Design, test and integrate metrology software for the EUV scanners
2012 - 2014  Senior Physics Development Engineer ASML / TMC, Architect / Developer / Integrator of the metrology layer in the EUV sources
2015 -  Senior Physics Development Engineer ASML / TMC, functional designer and integrator of the Yieldstar Focus Application group