To my loving parents
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<tr>
<td>DMS</td>
<td>Dilute magnetic semiconductor</td>
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<tr>
<td>EFG</td>
<td>Electric field gradient</td>
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<td>ESR</td>
<td>Electron Spin Resonance</td>
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<td>GaAs/Sap</td>
<td>Gallium Arsenide on Sapphire</td>
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<td>GUI</td>
<td>Graphical user interface</td>
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<td>LED</td>
<td>Light emitting diode</td>
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<td>LIQR</td>
<td>Light induced quadrupolar relaxation</td>
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<td>LT-MBE</td>
<td>Low temperature molecular beam epitaxy</td>
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<td>MPL</td>
<td>Magneto-photoluminescence</td>
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<td>NIR</td>
<td>Near infrared</td>
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<td>NMR</td>
<td>Nuclear magnetic resonance</td>
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<td>OLE</td>
<td>Object linking and embedding</td>
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<td>OPNMR</td>
<td>Optically pumped nuclear magnetic resonance</td>
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<tr>
<td>QTH</td>
<td>Quartz-Tungsten-Halogen lamp</td>
</tr>
<tr>
<td>QWP</td>
<td>Quarter waveplate</td>
</tr>
<tr>
<td>PMT</td>
<td>Photomultiplier tube</td>
</tr>
<tr>
<td>RF</td>
<td>Radiofrequency</td>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
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<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>USB</td>
<td>Universal serial bus</td>
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<td>XRD</td>
<td>X-ray diffraction</td>
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Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

OPTICALLY PUMPED NUCLEAR MAGNETIC RESONANCE INVESTIGATION OF STRAIN AND DOPING EFFECTS IN GALLIUM ARSENIDE

By

John T. Tokarski III

May 2019

Chair: Clifford R. Bowers
Major: Chemistry

This work focuses on employing the use of elastic strain or doping to increase the nuclear spin polarization that results after optical pumping in GaAs. Usually, in III-V semiconductors, the optically induced conduction electron spin polarization is limited to 50% of the maximal value. By incorporating strain or dopants into the system, we aimed to lift degeneracies within the electronic band structure to increase the conduction electron spin polarization. Strain was induced via epoxying bulk GaAs to a Si or Sapphire wafer. Cooling the sample down to cryogenic temperatures caused differential thermal contraction, and thus strained the GaAs. A theoretical bending model is presented to describe how the strain relaxes in these composite materials. Moreover, the local strain at the surface and interface are investigated and facilitate in approximating the optical absorption spectrum. In the case of doping, we investigated the magnetic semiconductor Ga$_{1-x}$Mn$_x$As (where x=0.01 or 0.038). In this sample, we investigated the optically enhance NMR signal and report our findings. Additionally, all experiments were conducted in a homebuilt superfluid He compatible OPNMR probe. The OPNMR probe is novel because it incorporates the use of optics within the cold space.
CHAPTER 1
NUCLEAR MAGNETIC RESONANCE & OPTICALLY PUMPED NUCLEAR MAGNETIC RESONANCE

This work focuses on nuclear magnetic resonance spectroscopy and therefore, this chapter will act as an introduction to fundamental concepts. Pertinent topics to this research are covered including, the Zeeman interaction, the quadrupolar interaction and the hyperfine interaction. Furthermore, the principles of polarization and hyperpolarization are described including mechanisms like the Overhauser effect and lastly optical pumping.

Introduction to Nuclear Magnetic Resonance

All matter is comprised of atoms with intrinsic properties such as mass, charge and spin. The last of these is less recognized but nonetheless very important. Spin is a form of angular momentum, completely removed from other forms of angular momenta (e.g. orbital, rotational) and is a quantum mechanical phenomenon. Nuclei and electrons both have spin and despite its name, spin does not arise from actual physical rotation of the particle but from intrinsic angular momentum. In this work, the nuclear and electronic spin will be denoted as \( I \) and \( S \), respectively.

Classically, magnetism between matter and a magnetic field can be described as the interaction of a magnetic moment vector, \( \vec{\mu} \), with magnetic field \( \vec{B} \),

\[
E = -\vec{\mu} \cdot \vec{B}
\]  

(1-1)

This microscopic magnetism is directly related to the spin. According to the Wigner-Eckhard theorem, the nuclear spin angular momentum and magnetic moment are related by the following\(^1\):

\[
\hat{\mu} = \gamma \hat{I}
\]  

(1-2)
where $\hat{\mu}$ is the magnetic moment operator, $\hat{I}$ is the nuclear spin operator and $\gamma$ is the gyromagnetic ratio. For an ensemble of $N$ spins, the individual magnetic moments can couple to each other and result in net magnetization $\hat{M}_{\text{net}}$ given by:

$$\hat{M}_{\text{net}} = \sum_{i} \hat{m}_i$$

The net magnetization is the observable quantity in our experiments. Interestingly, as apparent from Equations 1-1 through 1-3, the macroscopic observable elucidates information about the quantum mechanical nuclear spin.

When situated in a magnetic field, the nuclear magnetic moments are not static. Instead the nuclear magnetic moments precess about the magnetic field, analogous to a toppling spinning top. The frequency of the precession $\omega_0$, known as the Larmor frequency, is equal to:

$$\omega_0 = -\gamma B_0$$

where again $\gamma$ is the nuclear gyromagnetic ratio, and $B_0$ is the magnetic field strength.

In a nuclear magnetic resonance (NMR) experiment, the net magnetization is colinear with the direction of the magnetic field. For simplicity, we place the field along the $z$-axis of a Cartesian coordinate system. The net magnetization can be rotated away from the $z$-axis, into the $xy$-plane using a pulsed oscillating magnetic field, $B_1$. To efficiently rotate the magnetization into the $xy$-plane, the pulsed field frequency must be equal to the Larmor frequency.

When $\hat{M}_{\text{net}}$ is rotated into the $xy$-plane and $B_1$ is off, the nuclear magnetic moments will resume precession about the static field $B_0$, thereby causing $\hat{M}_{\text{net}}$ to
oscillate about $B_0$. In the NMR experiment, the sample is placed in a coil, so the oscillating magnetization may induce a current in the coil. The current is collected as a function of time and referred to as the signal. The signal undergoes a mathematical transformation known as a discrete Fourier Transform, which decomposes the time dependent signal into the individual frequency components that collectively result in the signal. The subsequent data is the NMR spectrum in the frequency domain.

**Zeeman Interaction**

At the quantum level, for a nucleus with total spin $I$, there are $2(I+1)$ eigenstates. The eigenstates denoted as $M$, range from $I$ to $-I$ in integer steps. For example, the nucleus of interest in this work is Ga-71, which has $I = \frac{3}{2}$, and has $M = \left\{ \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2} \right\}$. In the absence of a magnetic field, the eigenstates are degenerate. However, these degeneracies are broken with the application of a strong magnetic field according to the Zeeman effect which is depicted in Figure 1-1.

![Energy splitting diagram of the Zeeman eigenstates with increasing magnetic field](image)

Figure 1-1. The energy splitting diagram of the Zeeman eigenstates with increasing magnetic field.
The Hamiltonian of the Zeeman effect is defined as

\[ \hat{H}_Z = \gamma B_0 \hat{I}_z \]  

(1-5)

\[ \hat{I}_z |I, M \rangle = M |I, M \rangle \]  

(1-6)

where the product \( \gamma B_0 \) is the Larmor frequency, \( \hat{I}_z \) is the projection along the z-axis of the nuclear spin angular momentum operator which is defined in Equation 1-6. Note, Equation 1-5 is in units of frequency. For convenience, all future Hamiltonians will be written in units of frequency, missing a factor of \( \hbar \). In the NMR experiment, the transitions from \( M \rightarrow M \pm 1 \) are probed.

**Nuclear Quadrupolar Interaction**

Nuclei with total spin \( I \geq 1 \) are referred to as quadrupolar nuclei, which couple the electric quadrupole moment of the nucleus to external electric field gradients generated by surrounding orbiting electrons. The full nuclear quadrupole Hamiltonian is defined as\(^1\)

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

(1-7)

where \( e \) is the elementary charge, \( Q \) is the nuclear quadrupolar moment, \( I \) is the nuclear spin quantum number, \( \hat{I} \) is the nuclear spin operator, and \( \mathbf{V} \) is a second rank tensor called the electric field gradient. In the case where the quadrupolar interaction is much smaller than the Zeeman interaction, the secular approximation to the first order is sufficient to describe the nuclear quadrupole Hamiltonian. The first order quadrupolar Hamiltonian may be written as\(^1\)
\[ \hat{H}_Q^I = \omega_Q^I \frac{1}{6} (3\hat{I}^2 - I(I+1)\hat{I}) \]  
(1-8)

\[ \omega_Q^I = \frac{3eQV_{zz}}{2I(2I-1)\hbar} \]  
(1-9)

where the \( \omega_Q^I \) is the quadrupolar coupling constant, \( V_{zz} \) is the z-component of the electric field gradient in the principal axes, and \( \hat{I} \) is the identity matrix. The coupling of the Zeeman interaction and quadrupolar interaction is described by

\[ \hat{H} = \hat{H}_z + \hat{H}_Q^I \]  
(1-10)

\[ \hat{H} = \omega_d \hat{I}_z + \omega_Q^I \frac{1}{6} (3\hat{I}^2 - I(I+1)\hat{I}) \]  
(1-11)

Note the use of the matrix notation in Equations 1-8 and 1-11. The matrix form of the Zeeman and quadrupolar interactions is given below, where the first term is the Zeeman interaction and the quadrupolar interaction is the second term.

\[
H = \begin{bmatrix}
\frac{1}{2} \omega_0 & 0 & 0 & 0 \\
0 & \frac{1}{2} \omega_0 & 0 & 0 \\
0 & 0 & \frac{1}{2} \omega_0 & 0 \\
0 & 0 & 0 & \frac{1}{2} \omega_0 \\
\end{bmatrix}
+ \begin{bmatrix}
\frac{1}{2} \omega_Q & 0 & 0 & 0 \\
0 & \frac{1}{2} \omega_Q & 0 & 0 \\
0 & 0 & \frac{1}{2} \omega_Q & 0 \\
0 & 0 & 0 & \frac{1}{2} \omega_Q \\
\end{bmatrix}
\]  
(1-12)

\[
= \begin{bmatrix}
\frac{1}{2} \omega_0 + \frac{1}{2} \omega_Q & 0 & 0 & 0 \\
0 & \frac{1}{2} \omega_0 - \frac{1}{2} \omega_Q & 0 & 0 \\
0 & 0 & \frac{1}{2} \omega_0 - \frac{1}{2} \omega_Q & 0 \\
0 & 0 & 0 & \frac{1}{2} \omega_0 + \frac{1}{2} \omega_Q \\
\end{bmatrix}
\]

In practice, the quadrupolar interaction manifests itself in the NMR lineshape by additional resonances. For example, for \( I = 3/2 \) (e.g. Ga-71), the single peak will
become a triplet. This is visually depicted in the Figure 1-2 by the energy diagram and the stick plot of the NMR signal.

Figure 1-2. Left: The energy splitting diagram of the Zeeman eigenstates coupled with a quadrupolar coupling constant $\omega_Q^i$. Right: A stick plot of the NMR spectrum of the energy diagram.

**Hyperfine Interaction**

Another important interaction discussed in this work is the hyperfine interaction. This interaction describes the coupling of electronic spins to nuclear spins. The hyperfine Hamiltonian is defined as

$$\hat{H}_{HF} = A \hat{I} \cdot \hat{S} = A \left[ \frac{1}{2} \left( \hat{I}_+ \cdot \hat{S}_- + \hat{I}_- \cdot \hat{S}_+ + \hat{I}_z \cdot \hat{S}_z \right) \right] \quad (1-13)$$

where $A$ is the hyperfine coupling constant, the operators $\hat{I}$ and $\hat{S}$ correspond to the nuclear and electronic spin operators (where the electron spin operator is analogous to the nuclear spin operator). The first term in the square brackets of Equation 1-13 includes the use of the ladder operators, $\hat{I}_\pm$ and $\hat{S}_\mp$, which allow for mutual spin flip-flops to occur between the nucleus and coupled electron. Lastly, the term $\hat{I}_z \cdot \hat{S}_z$ allows for
static effects to occur, such as a shift in the observed frequency in the NMR spectrum, known as the Knight shift. The hyperfine coupling constant is defined as

\[ A = \frac{16\pi}{3} \mu_B \hbar \gamma_0 |\psi(r)|^2 \]  

(1-14)

where \( \mu_B \) is the Bohr magneton, \( \psi(r) \) is the wavefunction of the electron at displacement \( r \) from the nucleus, \( \gamma \) is the nuclear gyromagnetic ratio, and \( \nu_0 \) is the volume of the unit cell. Note that in Equation 1-14, the term \( |\psi(r)|^2 \) is the probability density of the electron at the displacement \( r \), therefore highly localized electrons with shorter displacements will lead to maximal values of \( A \).

**Polarization and the Overhauser Effect**

According to Boltzmann statistics, a system at thermodynamic equilibrium will have a greater relative population difference with larger energy differences between levels. For example, a two-level system with no degeneracies has a population difference called its polarization. The polarization, \( P \), for a two-level system is defined as

\[ P = \frac{e^{-E_\beta/kT} - e^{-E_\alpha/kT}}{e^{-E_\beta/kT} + e^{-E_\alpha/kT}} \]  

(1-15)

\[ P = \tanh \left( \frac{\Delta E}{2kT} \right) \]  

(1-16)

where \( E \) is the energy associated with levels \( \alpha \) and \( \beta \), \( k \) is the Boltzmann constant, and \( T \) is the temperature. Equation 1-15 is also equivalent to 1-16, in which the polarization is the hyperbolic tangent of the energy difference divided by the Boltzmann factor. From Equations 1-15 and 1-16, if the energy differences are small compared to
$kT$, then there will be little difference in populations. Note that this has been written for a two-level system with no degeneracies. For a spin-3/2 system (e.g. Ga-71), the polarization is defined as:

$$P = \frac{I_z}{I} = \left(\frac{1}{2} \text{Tanh} \left(\frac{\hbar \gamma B}{2kT}\right) + \text{Tanh} \left(\frac{\hbar \gamma B}{kT}\right)\right)^{3/2}$$

(1-17)

As evident from Equation 1-17, two parameters can be modified to increase the polarization: magnetic field strength and temperature. Currently, the world’s strongest persistent magnetic field is 45 T, and the gyromagnetic ratio of Ga-71 is 81.731 $(2\pi$ MHz)/T. The associated energy for the described system is much less than the energy from the surroundings at room temperature and results in extremely low spin (approximately $1.5 \times 10^{-5}$). Decreasing the temperature of the system is another viable method to increase the thermal polarization. However, for low $\gamma$ nuclei, this may require extremely low temperatures as depicted in Figure 1-3. The expectation value of $I_z$ is plotted as a function of temperature in a 3.00 T magnetic field (the field used predominantly in this work). As evident from the plot, the temperature needs to be in the mK regime to generate any sizable increase in polarization, and to fully polarize the system, it would require the temperature to be 1 mK or less. Importantly, the $T_1$, the characteristic time constant that describes the rate for the nuclear spin system to reach equilibrium, becomes excessively long at low temperatures. Therefore, at the fields used in this work, it would take roughly 35 hours to reach thermal equilibrium for GaAs.
Thanks to the pioneering works of Overhauser, Carver and Slichter, the important effects of electronic-nuclear hyperfine coupling led to a mechanism that could enhance nuclear spin polarization well beyond thermal equilibrium.\textsuperscript{7-9} Overhauser theoretically showed that nuclei in a metal could be dynamically polarized via its conduction electrons when irradiated with microwaves near the Larmor frequency of the conduction electron.\textsuperscript{7} Months before Overhauser's publication, Carver and Slichter were the first to observe this effect by saturating the electron spin resonance (ESR) transition of conduction electrons with continuous irradiation with microwaves, and subsequently detecting enhanced $^7$Li NMR signals in metallic Li.\textsuperscript{9}
Figure 1-4. Schematic of the Overhauser effect of a spin-$\frac{1}{2}$ system. The ket notation is as follows: the first arrow indicates the electronic spin state, and the second arrow indicates the nuclear spin state. Nearly horizontal levels are nuclear spin transitions and detected via NMR, while vertical levels are electronic spin transitions and detected with ESR.

The underlying mechanism of the Overhauser effect stems from population imbalance. In the Overhauser effect seen in Figure 1-4, the ESR transition is saturated via microwave irradiation. The conduction electron attempts to return to equilibrium and one viable route is the hyperfine interaction. The conduction electron can undergo a hyperfine mediated cross relaxation mechanism which allows the electron to relax by flipping a nuclear spin. This mutual spin flip is normally not allowed according to the selection rules, but due to the ladder operators in Equation 1-13, the transition $M_I + M_S = 0$ is allowed.\(^1\) If the electrons are saturated for long periods of time, large nuclear spin polarization can accumulate and lead to enhanced NMR signals. The
overall enhancement is governed by the ratio $\frac{\gamma_S}{\gamma_I}$, the ratio of the gyromagnetic ratios of the electron and the nucleus.

**Optically Pumped Nuclear Magnetic Resonance**

Lampel was the first researcher to demonstrate an optical Overhauser effect. In his experiments, silicon was cooled to 77 K and irradiated with unpolarized or circularly polarized light from a xenon lamp. Unlike the traditional Overhauser effect — where the electron spins are saturated with nearly resonant microwaves — the optical Overhauser effect generates conduction electrons via optical excitation and are initially in a non-equilibrium state. However, the lifetime of the conduction electron is shorter than the conduction electron’s longitudinal relaxation time ($T_{1e}$). Therefore, the system never thermalizes and remains in a non-equilibrium state without microwave irradiation. Furthermore, Lampel found that larger nuclear spin polarizations could be achieved by using circularly polarized light. In the case of unpolarized light, conduction electrons are not polarized (i.e. $s_z = 0$). Circularly polarized light can generate spin-polarized conduction electrons that deviate further from equilibrium and thereby polarize nuclei more efficiently.

The groundbreaking work of Lampel was furthered with the work of Barrett and coworkers in 1994 as they directly detected the same optical Overhauser effect in a GaAs/AlGaAs quantum well thin film. In their work, they observed a temperature-dependent Knight shift, and measured a g-factor equal to -0.49. Furthermore, they detected quadrupolar splitting in their “optically pumped” NMR (OPNMR) experiments. They attributed this splitting from Ga nuclei positioned in the barriers of the quantum well, where the AlGaAs alloy has an associated non-zero electric field gradient. Lastly,
they found that the OPNMR signal was largely dependent on the photon energy. In this work, they attempted to correlate the magneto-photoluminescence (MPL) with the OPNMR signal and saw moderate agreement at low photon energies. At higher photon energies, the discrepancies between the MPL and OPNMR signal increased. The explanation they posited was that the two techniques probe two different physics. In the MPL, a photon is absorbed, and subsequently the excited carrier relaxes to a radiative state, followed by radiative recombination. In the OPNMR experiment, a photon is absorbed as well, but the carrier relaxes to a nonequilibrium spin state, which does not necessitate radiative recombination.

The first detection of OPNMR in bulk GaAs was in 1996 by Pietraß and colleagues, who investigated different samples of GaAs, including semi-insulating, n-type and p-type.\textsuperscript{12} They also investigated the action spectra (OPNMR signal versus the photon energy) of the three samples and also saw that the OPNMR signal in the bulk was sensitive to the photon energy. Importantly, they noted that OPNMR signals were much larger below the band gap, and correctly attributed this to penetration depth effects. From optical absorption spectroscopy, it is known that typical optical penetration depths of photons at or above the band gap are about 800 nm for GaAs.\textsuperscript{13} Photons with energy below the band gap can penetrate farther into the sample and can probe a larger volume.\textsuperscript{14} Due to the increase in volume, the OPNMR signal below the band gap is larger, as more nuclei are hyperpolarized. Lastly, they investigated the temperature dependence of the OPNMR signal and saw that optical pumping was more efficient with decreasing temperature. They attributed this increase in efficiency to the longer lifetimes and spin relaxation times of the photoexcited electrons. Although this
may be correct, it most likely is not the dominant factor in this case, as will be shown later.

A year later, the seminal work conducted by Kuhns and co-workers investigated the magnetic field dependence of the OPNMR in bulk GaAs. From their work they found that the optically enhanced signals originate from a scalar hyperfine relaxation of electrons trapped at shallow donor sites. The cross-relaxation mechanism is efficient when the proximal nuclei experience a fluctuating hyperfine field at the shallow donors. The cross-relaxation rate, $1/T_{11}^{II}$ is derived as:

$$
\frac{1}{T_{11}^{II}} = \frac{S(S+1)}{3} \Gamma J_{ex} (\omega_l - \omega_s) e^{-r/a_0} \tag{1-18}
$$

where $S$ is the electron spin number, $\omega_l$ is the nuclear Larmor radial frequency, $\omega_s$ is the electronic Larmor radial frequency, $\Gamma$ is the probability of electron localization, $a_0$ is the Bohr radius, and $J_{ex}(\omega)$ is the spectral density function of the hyperfine interaction. Furthermore, in their model they included nuclear spin diffusion effects and nuclear spin relaxation. The master rate equation they derived was modified from Abragam:

$$
\frac{dI_z}{dt} = D V^2 I_z - \frac{1}{T_{11}^{II}} \left[ I_z - I_{eq} - \frac{I(I+1)}{S(S+1)} (S_z - S_{eq}) \right] - \frac{I_z}{T_{11}} \tag{1-19}
$$

where $D$ is the nuclear spin diffusion constant, $I_{eq}$ and $S_{eq}$ are the thermal equilibrium ensemble-averaged expectation values of the nuclear and electron spin respectively, and $T_1$ is the dark nuclear spin lattice relaxation time. The three terms in Equation 1-18 from left to right are: the nuclear spin diffusion term, the cross-relaxation term, and the spin-lattice relaxation term. The diffusion term allows nuclei far removed from the
shallow donors to be polarized. The cross-relaxation term is responsible for accruing polarization via the hyperfine interaction. This polarization should be initially localized near the shallow donors. And lastly, the spin lattice relaxation term places an upper limit on the total polarization as it drains polarization in the sample. Notably, this model demonstrated the importance of the conduction electron spin polarization and its deviation away from thermal equilibrium. In the limit of short pumping times where diffusion and other relaxation mechanisms can be neglected, Equation 1-19 can be approximated as

\[
\frac{dI_z}{dt} \approx \frac{1}{T_1} \left[ \frac{I(I+1)}{S(S+1)} (S_z - S_{eq}) \right],
\]

where \( I_{eq} \) should be negligible. From 1-20, we can see that the OPNMR signal is directly proportional to the deviation from thermal equilibrium. The thermal equilibrium electron spin polarization is defined as \(^3\):

\[
S_{eq} = -\frac{1}{2} \tanh \left( \frac{\hbar g \mu_B B}{2kT} \right),
\]

where \( g \) is the electronic g-factor, and \( \mu_B \) is the Bohr magneton. As the temperature decreases, \( |S_{eq}| \) will increases until it is fully polarized (i.e. \( S_{eq}/S = 1 \)). Thus, the larger the thermal equilibrium spin polarization, the larger the deviations can be, and thus enhance the OPNMR signal. This important feature explains the temperature dependent results described earlier.

Currently, the OPNMR phenomenon has been studied in a multitude of materials including \( \text{InP}^{16-19}, \text{CdS}^{20}, \text{CdTe}^{21} \), and even \( \text{GaN}^{22} \). Although numerous materials show
optically enhanced signals, the work discussed in this dissertation will focus solely on 71-Ga signals of GaAs.

**The Photon Energy Dependence of the OPNMR Signal**

As noted from Barrett and Tycko's first observation of OPNMR in a quantum well sample, the OPNMR signal is strongly dependent on the photon energy used. However, there are two important factors to consider when investigating the photon energy dependence: the volume probed and the nuclear polarization. The OPNMR enhancement is largest below the band edge (1.519 eV at 1.5 K). This was originally seen by Pietraß and attributed to the penetration depth effect which changes the effective volume probed in the OPNMR experiment. Michal and Tycko investigated OPNMR signals in InP and performed stray-field NMR imaging of the polarization throughout the sample. Furthermore, they acquired multiple images as a function of photon energy to approximate the penetration depths of the incident photons. They found in their work that, although sub-band gap photons may give larger signals due to the larger penetration depth, the optical pumping efficiency is much lower. Furthermore, although the signals may be smaller, the optical pumping is much more efficient with photons at the band gap and above. In other words, sub-band gap photons lead to small nuclear spin polarization throughout the sample, and photons at and above the band gap result in high nuclear spin polarization localized only at the surface. This is consistent with other work performed in GaAs. The efficiency arises from \( \Gamma \), defined as the occupation probability of the shallow donor site, which is photon energy dependent. According to Paget, the dynamic polarization of GaAs occurs at shallow donors between the localized conduction electrons and proximal nuclear spins. The occupation probability of the shallow donor sites is given by,
where $\alpha$ is the absorption coefficient of photon energy $E$, $\tau_e$ is the lifetime of the conduction electron, $I$ is the laser intensity, $z$ is the displacement from the irradiated surface, and $N_D$ is the density of the shallow donors. From Equation 1-22, the photons below the band gap will have smaller occupancy factors compared to higher energy photons. This smaller occupancy factor changes the cross-relaxation rate in Equation 1-18, thereby changing the efficiency.

Lastly, oscillatory features are seen in the photon energy dependence of GaAs and other materials, specifically above the band gap. These oscillations arise from Landau quantization. The effect essentially discretizes the continuum of states in the valence and conduction bands into smaller sublevels. Consequently, the Landau levels further complicate the band structure, leading to a richer spin physics. This will be described in more depth in Chapter 2.

\[
\Gamma(z, E) = \frac{\alpha(E)\tau_e I}{N_D E} e^{-a(E)z}
\]  

Equation 1-22
CHAPTER 2
SEMICONDUCTOR BAND STRUCTURE AND THE EFFECTS OF STRAIN AND DOPING

The focus of this chapter is to investigate the relationship between the band structure of GaAs and the observed OPNMR signal. Therefore, the relevant semiconductor physics is introduced along with the band structure of GaAs. Furthermore, the onset of Landau level quantization will be explained and how it manifests into the action spectrum of the OPNMR signal. Furthermore, theoretical treatment of strain will be presented, as well as the effects of strain within the band structure. The chapter concludes with a description of the effects of doping on the band structure, specifically when doping with Mn.

Band Structure of Unstrained Bulk GaAs

In a crystalline semiconductor material, the electrons are bound within a lattice with a periodic potential. Wavefunctions that properly describe electrons bound within a weak periodic potential are known as Bloch wavefunctions with the form\(^{25}\)

\[
\psi_k(x) = U_k(x)e^{ikx},
\]  

(2-1)

where \(U_k(x)\) is the periodic function. The exponential term represents a travelling wave with crystal momentum \(k\). Note that Equation 2-1 is written in one dimension but can be applied to a three-dimensional crystal potential. Each solution of \(\psi_k\) corresponds to a particular value of \(k_0\), which corresponds to a state with energy \(E_k\). This relationship leads to E-k diagrams that graphically represent the band structure of materials. For GaAs, the simplified band structure near \(k = 0\) in the absence of an applied magnetic field is presented in Figure 2-1. The four curves shown in the figure correspond to the
conduction band, the heavy hole band, the light hole band and the split-off band. The latter three comprise the valence band. Figure 2-1 focuses on the $\Gamma$ valley of the band structure, where $E_g$ is referred to as the band gap. The band gap is lowest energy transition from the valence band to the conduction band. In Figure 2-1, the transition is exactly vertical in GaAs, and there is no change in $k$. Therefore, GaAs is said to be a direct band gap semiconductor. Another energy gap shown is $\Delta$, which is the energy difference between the split-off band and the top of the valence band. For GaAs, $E_g$ at 1.5 K is 1.519 eV and $\Delta$ is 0.341 eV.$^{26,27}$ For the photon energies described in this dissertation work (1.48-1.56 eV), transitions from the split-off band do not occur.

![Diagram of electronic band structure of GaAs](image)

Figure 2-1. The electronic band structure of GaAs near $k = 0$ which is also known as the $\Gamma$ valley.
Notably, the bands in the E-k diagram displayed in Figure 2-1 have a parabolic form. This arises from the dispersion relation
\[ E = \hbar \omega = \frac{\hbar^2 k^2}{2m^*}, \] (2-2)
where the energy $E$ is proportional to the square of the crystal momentum $k$.

Importantly, the denominator in Equation 2.2 has mass, $m^*$, which explains the names "heavy" hole and "light" hole. This mass in Equation 2-2 is the effective mass of the carrier. The effective mass can be related to the classical equation of motion by utilizing the group velocity, $v_g$, defined as
\[ v_g = \frac{1}{\hbar} \frac{dE}{dk}. \] (2-3)

Equation 2-3 shows that group velocity is related to the derivative of the E-k diagrams.

Furthermore, when an electric field is applied to the carrier, it experiences a force
\[ F_{\text{ext}} = eU, \] (2-4)
where $e$ is the elementary charge and $U$ is the electric field. However, scattering mechanisms (such as collisions with lattice vibrations) reduce the kinetic energy. Therefore during small time intervals between scattering events, the carrier moves a distance $v_g \delta t$ and gains energy
\[ \delta E = F_{\text{ext}} v_g \delta t \] (2-5)
\[ \frac{1}{v_g} \frac{dE}{dt} = \frac{\hbar}{\delta t} \frac{dk}{dt} = F_{\text{ext}}. \] (2-6)
Equations 2-5 and 2-6 show the relationship between the effective external force and the crystal momentum. The right side of Equation 2-6 can be reformulated to the classical equation of motion \( F = ma \),

\[
\hbar \frac{dk}{dt} = m^* a = m^* \frac{dv^*_z}{dt}.
\]  

(2-7)

where the acceleration can be re-written with respect to the time derivative of the group velocity. Finally, by substituting Equation 2-3 into Equation 2-7, the effective mass can be obtained from the relationship

\[
\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2}.
\]  

(2-8)

Equation 2-8 shows the very important relationship that the effective mass of the carrier is inversely proportional to the curvature of the E-k diagram. Thus, the heavy hole has lower curvature than the light hole band.

**Optical Selection Rules**

The most important step in the OPNMR experiment is optical absorption of photons to generate non-equilibrium conduction electron spin polarization, \( S_z \). As mentioned in Chapter 1, the larger the deviation from the equilibrium spin polarization, \( S_{eq} \), the greater the OPNMR enhancement. This was emphasized in Equation 1-20:

\[
\frac{dI_z}{dt} \approx \frac{1}{T_1} \left[ \frac{I(I+1)}{S(S+1)} \left( S_z - S_{eq} \right) \right].
\]  

(2-9)

The optically pumped conduction electron spin polarization, \( S_z \), is defined as,\(^{29}\)
\[ S_z = \frac{S_z^0}{1 + \frac{\tau}{T_{1,e}}} \]  

where \( S_z^0 \) is the initial optically induced spin polarization, \( \tau \) is the lifetime of the electron and \( T_{1,e} \) is the electronic spin relaxation time. The initial optically induced spin polarization is given by,

\[ S_z^0 = \frac{1}{2} \frac{\alpha_{+1/2} - \alpha_{-1/2}}{\alpha_{+1/2} + \alpha_{-1/2}} \]  

where \( \alpha_{+1/2} \) and \( \alpha_{-1/2} \) are the optical absorption coefficients for transitions to \( m_s = 1/2 \) and \( m_s = -1/2 \) conduction electron spin states, respectively. The relative transition rates at \( k = 0 \) are displayed in Figure 2-2. For example, when irradiating with \( \sigma^+ \) light, populating the state \( m_s = -1/2 \) is three times more likely than populating \( m_s = 1/2 \), resulting in \( S_z^0 = -0.25 \). In general, the optical selection rules for cubic crystals are \( \sigma^+ = \mp 0.25 \). Importantly, the maximal \( S_z^0 \) that can be induced in GaAs is limited to 50% of the maximum possible value of \( S_z \).

**Landau Quantization and Landau Levels**

A charged particle in the presence of a magnetic field will experience a Lorentz force. This also holds true for carriers in a semiconductor such as GaAs. The Schrödinger equation in the effective-mass approximation is given by

\[ \frac{1}{2m^*} \left( \hat{p} + \frac{e}{c} A \right)^2 \psi = E \psi \]  

\[ (2-12) \]
Figure 2-2. The optical selection rules for GaAs at $k = 0$ for different polarizations of light.

where $\hat{p}$ is the momentum operator, $e$ is the elementary charge, $c$ is the speed of light, and $A = \frac{1}{2}(\vec{B} \times \vec{r})$ is the vector potential. In our experimental setup, the laboratory frame has the magnetic field along the $z$-dimension, which is parallel to the growth direction of the semiconductor. Therefore, Equation 2-12 will have the form

$$
\frac{1}{2m_e} \left[ \left( \hat{p}_x - \frac{qB_0}{2c} \hat{y} \right)^2 + \left( \hat{p}_y + \frac{qB_0}{2c} \hat{x} \right)^2 + \hat{p}_z^2 \right] \psi = E \psi .
$$

The solution to Equation 2-13 was first obtained by Lev Landau in 1930. The solutions can be represented by a 2-D harmonic oscillator, where the quantized levels are known as Landau Levels. The energy eigenstates for the photoexcited electrons are

$\sigma^+ \text{ Photons } \rightarrow -0.25$

$\sigma^- \text{ Photons } \rightarrow +0.25$

$\pi \text{ Photons } \rightarrow 0$
\[ E_i = \left( n + \frac{1}{2} \right) \hbar \omega_c + \frac{\hbar^2 k_i^2}{2m} \]  

(2-14)

where \( n \) is the Landau quantum number, \( \omega_c \) is the cyclotron resonance frequency which is defined as \( \omega_c = eB_0/cm^* \) (in CGS units). The Landau levels increase linearly with magnetic field as exhibited in Figure 2-3.

![Figure 2-3. The magnetic field dependence of the first four Landau sublevels.](image)

The selection rules for direct interband transitions allow only \( \Delta n = 0 \). These transitions appear in the magneto-absorption spectrum, where transitions from the valence band to the conduction band will exhibit peaks between the different magnetic
sublevels. This effectively causes oscillations in the absorption above the nominal band edge.\(^{32}\)

Note, the above formulation has neglected the effects of spin. Equation 2-14 can be rewritten to account for the Zeeman effect as\(^ {33}\)

\[
E_i = \left( l + \frac{1}{2} \right) \hbar \omega_c + \frac{\hbar^2 k_x^2}{2m_e} + \frac{1}{2} g \mu_B B_0
\]

(2-15)

where \( g \) is the electronic g-factor, \( \mu_B \) is the Bohr magneton, and \( B_0 \) is the magnetic field. In GaAs, where the g-factor is relatively small for the conduction band (\( g = -0.44 \)), the Zeeman splitting of the conduction band is also relatively small compared to the splitting of the Landau levels.\(^ {33}\) However, in the valence band, the p-like orbitals (\( L = 1 \)) give rise to spin-orbit coupling at the \( \Gamma \) valley. The spin-orbit coupling between the spin-states are resolvable via OPNMR when varying the photon energy.\(^ {23, 33}\) The spin-orbit coupling in the valence band is related to the Luttinger parameters, which effectively increase the Zeeman splitting, as described by Sanders and co-workers.\(^ {34}\) The net result of Landau level formation is that it removes the continuum of states and results in a photon energy-dependent conduction electron spin polarization (i.e. \( S_0^z \) is no longer restricted to only \( \pm 0.25 \) above the band gap).

**Strain in Crystalline GaAs**

Strain is defined as a relative displacement and can be used to quantify the deformation of the lattice in a crystalline semiconductor. More generally, the strain, \( \varepsilon \), can be expressed as a tensor quantity:
In the case of a cubic crystal symmetry, Equation 2-16 can be reduced because permutations of the indices have the same value (i.e. \( \varepsilon_{yx} = \varepsilon_{xy} \)). Using the reduced notation, the elements of stress tensor, \( \sigma \), can be expressed in terms of the elements of the strain tensor by\(^{35}\)

\[
\sigma_{kl} = \sum_{ij} C_{ijkl} \varepsilon_{ij} \quad i, j, k, l = x, y, z ,
\]

where \( C_{ijkl} \) is the fourth-order stiffness tensor. For our purposes, it is convenient to work with the inverse of the stiffness tensor, which is known as the compliance tensor, \( S_{ijkl} \), and relates strain to stress by

\[
\varepsilon_{ij} = \sum_{kl} S_{ijkl} \sigma_{kl} .
\]

For the case of a cubic crystal structure, the high symmetry reduces the compliance tensor from 21 unique elements to three elements. Consequently, the strain can be defined as\(^{35}\)

\[
\begin{bmatrix}
\varepsilon_{xx} \\
\varepsilon_{xy} \\
\varepsilon_{xz} \\
\varepsilon_{yx} \\
\varepsilon_{yz} \\
\varepsilon_{zx}
\end{bmatrix} =
\begin{bmatrix}
S_{11} & S_{12} & S_{12} & 0 & 0 & 0 \\
S_{12} & S_{11} & S_{12} & 0 & 0 & 0 \\
S_{12} & S_{12} & S_{11} & 0 & 0 & 0 \\
0 & 0 & 0 & S_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & S_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & S_{44}
\end{bmatrix}
\begin{bmatrix}
\sigma_{xx} \\
\sigma_{yy} \\
\sigma_{zz} \\
\sigma_{yx} \\
\sigma_{yz} \\
\sigma_{zx}
\end{bmatrix} .
\]

In later chapters, experiments will focus on the strain that results from the application of equal stresses along the x and y directions of the sample (resulting in
biaxial strain). In this case, $\sigma_{xx} = \sigma_{yy} \equiv \sigma$. Furthermore, since no stress is applied along $z$, $\sigma_{zz} = 0$. One obtains

$$
\varepsilon_{xx} = \varepsilon_{yy} = (S_{11} + S_{12}) \sigma
$$

and

$$
\varepsilon_{zz} = 2S_{12} \sigma.
$$

Hence

$$
\varepsilon_{zz} = \frac{2S_{12}}{S_{11} + S_{12}} \varepsilon_{xx}.
$$

This relationship is important as it draws the relation between the in-plane strain and the out-of-plane strain. Chapters 5 and 6 use this relationship to quantify the amount of strain in GaAs via measurement of the nuclear quadrupolar splitting.

**Strain Effects on the Band Structure**

When strain is applied to a semiconductor, degeneracies in the band structure can be broken. The zincblende crystal structure of GaAs has 48 different symmetry operations. Due to the high symmetry of the crystal, the electronic wavefunctions are bound to exist with only certain eigenvalues which, giving rise to degeneracies amongst the valence bands. Strain can lower the symmetry and thus split the bands. Interestingly, in the case of hydrostatic strain (i.e. $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz}$), the symmetry does not change. Hence, hydrostatic strain conserves degeneracies within the valence band, but can shift the nominal band gap. In contrast, shear strain can deform the crystal symmetry and cause the valence bands to split. With respect to the conduction band, it is singly degenerate at the $\Gamma$ valley and does not split with strain.
Figure 2-4. The simplified band structures of GaAs when it is subjected to a biaxial compressive strain and tensile strain. The band gap for the tensile system is $E_{g,T}$, and for the compressive strain is $E_{g,C}$.

In the case of a biaxial strain, the strain can be decomposed into hydrostatic and shear components. Therefore, when a biaxial strain is applied to GaAs, the bands shift as shown in Figure 2-4. Notably, tensile strain reduces the effective band gap, while compressive strain increases it. In both cases of strain, however, the valence band degeneracy is lifted which can in principle allow $S_z$ to approach its maximum possible value of $\pm 1/2$.

**Doping Effects on the Band Structure**

Defects are usually added to semiconductors to modify the electronic properties of the material for device fabrication. Although there are numerous types and classifications of defects, this work will focus on substitutional point defects generally known as doping. For example, consider replacement of a Ga atom in the lattice of GaAs with a Si atom ($\text{Si}_{\text{Ga}}$). The Si atom has an extra valence electron and proton compared to the Ga atom. The Coulomb potential between the extra valence electron
and the extra charge of the Si nucleus is screened by its core electrons and the surrounding valence electrons within the crystal. Therefore, this extra valence electron is loosely bound to the Si atom within the GaAs and is easily ionized via thermal or electrical excitations.\textsuperscript{37} This electron acts as a donor to the system. Additionally, replacement of an As atom with a Si atom (Si\textsubscript{As}) would lead to an electron deficiency and would introduce an extra hole. This type of impurity would be an acceptor.

The Fermi level is defined as the energy at which an electron has 50\% probability of occupying either the conduction band or the valence band.\textsuperscript{25} The incorporation of impurities into the crystal can shift the Fermi level in the semiconductor up or down.\textsuperscript{25} Furthermore, impurity bands known as shallow donors or acceptors develop at the band edge, which effectively lower the band gap. However, because the dopants are generally considered point defects, the overall bulk lattice should remain unchanged, and hence, the symmetry should be conserved. Therefore, addition of dopants does not change the degeneracies in the band structure.

**Doping with Magnetic Ions in Semiconductors**

Doping with magnetic ions like manganese (Mn) leads to interesting electrical and magnetic properties.\textsuperscript{37-39} These are ideal for possible spintronics applications where the material has high magnetic order and semiconducting properties. Proposed devices would include non-volatile magnetic memory.\textsuperscript{40} The magnetic properties in materials are slightly tunable by adjusting the Mn concentration. Doping with magnetic ions is difficult, as the solubility into the system is not high.\textsuperscript{40, 41} However, recent advances in molecular beam epitaxy (MBE) techniques has yielded multiple magnetic semiconducting materials including GaMnAs,\textsuperscript{42-45} and InMnAs\textsuperscript{34}. Chapter 4 of this
dissertation focuses on GaMnAs where the Mn substitutes for Ga within the crystal (Mn\textsubscript{Ga}).

Interestingly, the p-d interaction is significant in GaMnAs and gives rise to a large-spin orbit coupling which can possibly split the valence band degeneracy.\textsuperscript{39} However, recent work suggests that an impurity band exists between the valence and conduction bands, where the impurity band arises from the localized d-states.\textsuperscript{46} Yet, other work within the field suggests that no impurity band exists.\textsuperscript{41} In the case where no impurity band exists, the band structure was similar to bulk GaAs.\textsuperscript{41} Ideally, if no impurity band exists, the larger spin-orbit coupling could lead to larger spin-splitting amongst the valence bands, thereby lifting the degeneracies. In the case of OPNMR, breaking the degeneracies within the valence band can lead to spin selective optical pumping, as investigated in Chapter 4.
CHAPTER 3
EXPERIMENTAL INSTRUMENTATION AND COLD OPTICS PROBE

In this chapter, the design, fabrication and performance of a unique “cold optics” OPNMR probe is described. As mentioned in Chapter 1, lower temperatures can enhance the efficiency of optical pumping. Therefore, a probe was designed to reach superfluid helium temperatures (less than 2.17 K), to increase OPNMR signals. Due to the construction of the cryostat used, light could be introduced into the system only via optical fiber. Therefore, polarizing optics were installed into the probe to polarize light in the cold space. Furthermore, the automated acquisition of the OPNMR action spectra is presented.

Motivation

In OPNMR, a conduction electron relaxes via a hyperfine induced cross relaxation that transfers spin angular momentum from the electron to proximal nuclei.\(^3\),\(^16\),\(^47\),\(^48\) This cross-relaxation mechanism occurs at low temperatures, typically below 40 K for GaAs.\(^49\) As the temperature is decreased, the hyperpolarization rate increases and allows for larger nuclear spin polarizations and more intense NMR signals.\(^23\),\(^33\) This will continue until the conduction electron’s thermal spin polarization is fully polarized (i.e. when \(kT \leq g \mu_B B\)), as seen in Figure 3-1. Hence, it is tremendously advantageous to decrease the temperature as the signal intensity will increase. This motivated us to design and fabricate an OPNMR probe suitable for superfluid \(^4\)He use to reach temperatures that approach a fully spin polarized state.
Figure 3-1. The thermal equilibrium expectation value of $S_z$ for GaAs ($g = -0.44$) in a 3.00 T magnet as function of temperature.

Unfortunately, many research cryostats do not readily come with optical access to the cold space. Furthermore, aligning a laser through a window, inside the bore of a magnet to impinge a 4x5 mm target is a cumbersome process. In addition, superfluid He preserves the polarization of NIR light, thus allowing for polarized light investigations. Normal liquid He has cavitations that can taint the polarization of the light. Therefore, we designed a superfluid OPNMR probe with a fiber-based polarization scheme. The operating concept involved an optical fiber terminating above polarization optics immersed in the superfluid bath to generate polarized light in the cold space. We describe here the design and performance of our adjustable superfluid cold optics OPNMR probe using the $^{71}$Ga OPNMR spectra of GaAs.
As illustrated in Figure 3-2, OPNMR and NMR experiments were conducted in a homebuilt optical NMR probe which was inserted into a Janis CDNT-NMR bath cryostat installed in an 89-mm high homogeneity 3.00 T Oxford superconducting magnet. The cryostat was filled with liquid $^4$He and mechanically pumped by a Leybold Sogevac SV 65 pump (not shown) to reach a base temperature of 1.5 K. The probe consists of a Q-dampened, series-matched LC circuit operating at 39.19 MHz (the Larmor frequency of Ga-71 at 3.00 T). To properly Q-dampen, we placed a 10 kΩ resistor in parallel with the
LC circuit to allow for some leakage current. As the temperature decreases, the conductivity of the resistor increases, allowing for more leakage current to maintain a broad bandwidth even at 1.5 K. The calibrated $\frac{\pi}{2}$ pulse was 5 µs (4 µs at cryogenic temperatures), giving an effective bandwidth of 100 kHz (125 kHz at cryogenic temperatures). The coil was affixed to a sapphire block, so the sample could be heat sunk to the sapphire using Apiezon N grease. The NMR spectra were acquired using a Tecmag Scout™ NMR Spectrometer. Temperatures were monitored via a Lakeshore Cernox™ temperature sensor. Laser light was focused into a multimode 0.540 mm core diameter fiber-optic cable (Thorlabs) that was fed into the probe and terminated above the cold optical polarizer. The cold optical polarizer consists of a 6-mm fused silica plano-convex lens (Thorlabs), a wiregrid polarizer (Meadowlark Optics) and an optically contacted zero-order quarter waveplate (Lambda Research Optics) mounted on a spur-gear pair (WM Berg). The helicity of the light can be continuously modulated from $\sigma^+$ to $\sigma^-$ by rotating the quarter waveplate via an aluminum rod that reaches from the cold space to the top of the probe.

**OPNMR Probe**

Similar to the design of Goto et al.,¹⁸ this OPNMR probe is a top-loading probe, and many of the electrical and mechanical connections are located at the top of the probe. The probe has 5 Ultratorr feedthroughs for the tuning and matching capacitor rods, the RF coaxial cable, the optical fiber and the rod for the quarter waveplate spur-gear coupler. Furthermore, there is a panel-mounted hermetically-sealed feedthrough for the temperature sensor. The probe body consists of a baffle stack of 5 copper disks. An important aspect in the probe design is the inclusion of holes drilled into the body of
the probe to prevent pressure gradients that generate thermo-acoustic oscillations (generally known as Taconis oscillations). These oscillations can cause pressure swings and temperature instability within the system. We found that drilling 2 holes with 2 cm spacing (starting from the top flange of the probe) prevented any oscillations from occurring as any pressure gradient along the body of the probe would be short-circuited to the rest of the cryostat.

![Figure 3-3](image.png)

Figure 3-3. On the left is a CAD drawing of the superfluid Helium probe built for the OPNMR experiments. To the right is the top of the probe, where all the electrical and mechanical feedthroughs are. The circuitry and probe head are shown in greater detail in Figure 3-4. Photo courtesy of author.

The probe head is shown in Figure 3-4. Depicted are the trimming capacitors, the fiber optic cable, the cold optics and the sapphire block that holds the coil for the sample. Notably, the cold optical polarizer is below the trimming capacitors of the NMR circuit. Typically, the distance between the trimming capacitors and the coil should be minimal to prevent spurious signals but due to spatial limitations and collimation concerns we chose the present arrangement. Moreover, because the operating frequency is low (39.19 MHz), and therefore the operating wavelength is so large, we
did not need to be concerned about the coil leads approaching \( \lambda/4 \) as they are only a few centimeters (while \( \lambda/4 \) is approximately 2 m). However, we do caution the that current arrangement at higher frequencies may not work. The coil leads (not pictured) allow for some parasitic capacitance which will limit the upper-limit of the operating frequency of the circuit. To date, the highest frequency achieved in this arrangement was 91.48 MHz using a 5-turn coil. Re-designing the configuration may be needed for higher frequencies.

Figure 3-4. Left: The probe head consisting of the two trimming capacitors (white cylinders) for the match and tune, the cold optical polarizer (outlined with a black square) and sapphire block that has the coil affixed to it. For clarity purposes, the fiber is shown illuminating the coil through the cold optical polarizer with red light. Right: The cold optical polarizer and the exploded view of the design, where A) is the collimating lens, B) is the collimating lens receptacle, C) is the receptacle for the wire grid polarizer, D) is the wire grid polarizer, E) is the quartz quarter waveplate, F) is the rotatable quarter waveplate receptacle and G) is the brass hub that is part of the housing.
Unlike single mode polarization-maintaining fibers which suffer from high attenuation, low throughput, and high sensitivity to local strains and stresses, we chose to use multimode fiber. We have found that multimode fiber affords the least amount of attenuation of the light and offers rigid stability despite the harsh conditions in our experiments. As depicted in the exploded view in Figure 3-4, light emerging from the fiber will be collimated by the planoconvex lens which is press-fitted into a homebuilt thin wall (0.035”) stainless steel receptacle. The collimated unpolarized light is then linearly polarized by the wire grid polarizer that is epoxied into a square slot under the collimating lens (Norland Optical Adhesive 81). The epoxy beads were laid at the corners of the polarizer to minimize the strain through the optical element upon cooling.

The linearly polarized light then passes through a zero-order optically contacted quarter waveplate (QWP). The optically contacted QWP was chosen because it allows for high optical power usage and, unlike traditional epoxied zero-order waveplates, no air gap is in between the waveplates that could freeze and obstruct the beam path. The QWP was epoxied to its thin wall receptacle with Norland Optical Adhesive 81. The thin wall receptacles were chosen to provide the least amount of mechanical stress to the optics, since differential thermal contraction will occur upon cooling and can change the optical response of the polarizing elements. Furthermore, when the receptacles were designed, extra clearance was allotted so that the thermal contraction of the stainless steel would be minimal and not compress the optics.

The QWP is a uniaxial crystal that can generate circularly polarized light if and only if its slow and fast axes are properly aligned with the incoming linearly polarized light. Therefore, the QWP needed to be rotatable in the cold space. The QWP
receptacle was spot welded to a 50-tooth spur gear, which was coupled to a 20-tooth gear on an aluminum rod that extends to the top of the probe and can be controlled via a knob at room temperature. A small amount of graphite was applied to the gears as lubricant. The QWP gear assembly was housed in a naval brass fitting with a hub for rotation of the gear. Outside of the probe, a turn counter was installed to the QWP rod, so that the exact location of the QWP could be known throughout the 2.5 turns required to fully rotate the element.

![Graph showing transmission spectra of the wire grid polarizer](image)

**Figure 3-5.** Transmission spectra of the wire grid polarizer subjected to cryogenic conditions and a 3.00 T magnetic field. Using a linear polarizer in conjunction with the wiregrid polarizer, the light was collected in two different arrangements, with the polarizers parallel (red) and crossed (blue). The results agree with Malus’s Law indicating that the element still linearly polarizes even at cryogenic temperatures.

**Performance**

Because the wire grid polarizer was not specified to low temperatures by the vendor, we investigated the performance in an Oxford continuous flow optical cryostat (CF-1200) at 3.8 K. In this experiment, we collected the profile of a Quartz-Tungsten-
Halogen lamp (QTH) with the wire grid polarizer placed after a linear polarizer. We measured the QTH profile with the linear polarizer parallel and crossed with respect to the wire grid polarizer. As depicted in Figure 3-5, the wire grid polarizer passed the linearly polarized light at cryogenic temperatures and rejected light polarized orthogonal to polarizer with a contrast ratio of roughly 100. Therefore, we found this polarizer suitable for our applications over the wavelength range of interest (790-830 nm).

![Figure 3-6. Ga-71 NMR spectra of GaAs. The black trace corresponds to the room temperature thermal NMR signal, while the blue and red traces are OPNMR spectra at 4.2 K and at 1.5 K, respectively. All spectra were recorded at 3.00 T. OPNMR spectra were recorded with 1.56 eV, unpolarized light with irradiation times of 8 minutes, single scan. The thermal scan was acquired with 16 scans and 5 s recycle delay.](image)

Next, we investigated the performance of the probe and confirmed that it behaves as designed. As depicted in Figure 3-6, the OPNMR signal is much larger at 1.5 K (red) compared to the signal acquired at 4.2 K (blue), as expected. The hold time of the superfluid He with the heat load of the probe and light is approximately 10 hours and shows no signs of temperature instability. Furthermore, when the QWP was rotated, the $^{71}$Ga signal was modulated corresponding to the angle of the QWP. Figure
3-7 shows the integral of the OPNMR signal properly produced a sinusoidal function as expected when rotating the QWP through its fast and slow axes. From this image, we could positively state that we successfully developed a variable cold optical polarizer suitable for superfluid He use.

![Figure 3-7. Top: Stack plot of the OPNMR spectra where the QWP was variably rotated. Bottom: The integral of the OPNMR signal plotted as a function of the QWP angle.](image-url)
**OPNMR Pulse Sequence**

Unless otherwise noted, all OPNMR spectra were collected with the pulse sequence shown in Figure 3-8. In this sequence, there are 3 notable sections: the saturation pulse comb, the OPNMR time ($\tau_L$) that allows for nuclear spin polarization to accrue, and the acquisition. In the first part of the sequence, an RF pulse is applied 16 times with 50 ms intervals between pulses. The effect removes any residual magnetization from the z-axis, and places it in the xy-plane. After 50 ms, any magnetization in the xy-plane should decohere, and this is repeated 16 times for thoroughness. At the end of the pulse comb, $I_z = 0$. During the interval $\tau_L$, nuclear spin polarization accumulates due to optical pumping. After the optical pumping time, another RF pulse is applied to rotate the magnetization in the xy-plane again, and the signal is acquired.

![Figure 3-8. Saturation-Recovery OPNMR pulse sequence](image)

**Laser Source**

The laser used in this work was a Coherent 899-01 Ring laser which uses a Ti:Sapphire gain medium to generate laser light from 1.4848-1.5694 eV. The pump laser is a Verdi-G 15 W solid state laser, which emits 532 nm light from 0.1-15 W. The
laser linewidth was measured to be 95 GHz. Linewidth measurements were carried out using a McPherson monochromator with 1200 grooves/mm and a 0.66 focal length. Furthermore, the Ti:Sapphire is tunable using a rotatable birefringent filter to produce a TEM$_{00}$ light beam over the entire tuning range. An optical diode is inserted in the cavity to prevent spatial hole burning in the gain medium.

**Labview Automation of Action Spectra**

Previously noted in Chapters 1 and 2 is the interest in probing the band structure of the sample by investigating the signal dependence on the photon energy. The plot of the OPNMR signal with respect to photon energy is called the action spectrum. The action spectra are very time consuming, but do not require frequent human intervention. Therefore, a Labview program was developed to automate the acquisition of the action spectrum. The overall scheme of the automation is to tune the laser to a wavelength, while maintaining constant optical power. Once tuned to the wavelength of interest and at the correct power, the automation initiates acquisition of the NMR spectrum. The program then saves the spectrum, tunes to a new wavelength, and repeats the loop until all wavelengths have been recorded.

To change wavelength and maintain constant power, a microcontroller Arduino UNO drives two different stepper motors. One stepper motor is connected to a birefringent filter on the laser that tunes the output wavelength. Despite being almost linear, the stepper motor was calibrated and fitted to a second-order polynomial. As seen in Figure 3-9, the residuals for a linear fit showed that a line did not accurately reproduce the data, but instead attempted to mitigate error. The second-order polynomial was chosen due to the goodness of fit and minimal residuals.
Figure 3-9. Calibration of the stepper motor to its corresponding wavelength emitted from the laser. On the left is the data fitted to a line and below are its residuals. On the right is the same data fitted to a second order polynomial and below are its corresponding residuals as well.

The other stepper motor adjusts a neutral density filter at the output of the laser to adjust the laser output. The reproducibility of the automation was verified using a McPherson 207 monochromator. The results showed that the automation remains reliable up to ±0.117 nm, which is much less than experimental step size (0.5 nm).
Figure 3-10. The Labview action spectrum automation featuring the Arduino that controls the two stepper motors. The output of the laser is shown with the red trace. The laser radiation passes through the neutral density filter and is reflected by a mirror through a glass slide to the fiber coupler. The glass slide reflects approximately 10% of the beam to the power meter which is read by Labview. Photos courtesy of author.

The experimental setup shown in Figure 3-10 includes a glass plate to reflect a small fraction (~10%) of the laser to a power meter, a Thorlabs thermopile. The analog output is sent to a National Instruments DAQ to be digitized and read by the Labview program. The feedback is used to adjust the laser output with the neutral density filter. Lastly, when the power is within an acceptable threshold, Labview opens the NMR software and begin the acquisition. Labview then waits the for the experiment to finish and repeats this process. If the laser intensity fails to converge, the experiment will be flagged in the automation post-report and visualized by an intensity plot in the GUI of the program.
Growth Information of Samples

Multiple samples of GaAs are investigated in this work. The majority of the work focuses on semi-insulating (i.e. undoped) GaAs (si-GaAs), while wafers of p-type GaAs (p-GaAs) and n-type GaAs (n-GaAs) were also studied. All three wafers were purchased from Wafer Technology Ltd. The wafers were all grown via vertical gradient freeze method (VGF) and had a double-sided polish, with a primary flat cut along the <0\bar{1}1> growth direction. Important growth information supplied by the vendor is included in Table 3-1.

Table 3-1. Growth properties of the si-GaAs, p-GaAs, and n-GaAs

<table>
<thead>
<tr>
<th>Property</th>
<th>si-GaAs</th>
<th>p-GaAs</th>
<th>n-GaAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orientation</td>
<td>(100) ± 0.03°</td>
<td>(100) ± 0.04°</td>
<td>(100) ± 0.04°</td>
</tr>
<tr>
<td>Thickness (μm)</td>
<td>363 ± 1</td>
<td>362 ± 7</td>
<td>365 ± 3</td>
</tr>
<tr>
<td>Resistivity (Ω cm)</td>
<td>2.50 E7</td>
<td>7.50 E-3</td>
<td>1.92 E-2</td>
</tr>
<tr>
<td>Hall Mobility (cm² V⁻¹ s⁻¹)</td>
<td>7320</td>
<td>93</td>
<td>2940</td>
</tr>
<tr>
<td>Carrier Concentration (cm⁻³)</td>
<td>3.50 E7</td>
<td>9.10 E18</td>
<td>1.08 E17</td>
</tr>
</tbody>
</table>

Additionally, specially grown samples of GaMnAs were also investigated in this work. These samples were prepared by Dr. Jacek Furdyna (Ga₀.⁹₆₂Mn₀.₀₃₈As) and Dr. Xinyu Liu (Ga₀.⁹₉Mn₀.₀₁As), who are both from the University of Notre Dame. The samples were characterized by our collaborators in the Khodaparast group at Virginia Tech, and their important material properties are given in Table 3-2.
Table 3-2. Growth properties of the GaMnAs samples. Growth layers indicate the layers beneath the film.

<table>
<thead>
<tr>
<th>Property</th>
<th>Ga$<em>{0.99}$Mn$</em>{0.01}$As</th>
<th>Ga$<em>{0.962}$Mn$</em>{0.038}$As</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film Thickness (μm)</td>
<td>0.800</td>
<td>7.8</td>
</tr>
<tr>
<td>Curie Temperature (K)</td>
<td>N/A (paramagnetic)</td>
<td>35</td>
</tr>
<tr>
<td>Hole Density (cm$^{-3}$)</td>
<td>-</td>
<td>1.0 E20</td>
</tr>
<tr>
<td>Growth Layers</td>
<td>Ga$<em>{0.99}$Mn$</em>{0.01}$As</td>
<td>Ga$<em>{0.962}$Mn$</em>{0.038}$As</td>
</tr>
<tr>
<td></td>
<td>Ga$<em>{0.68}$Al$</em>{0.32}$As (300 nm)</td>
<td>GaAs (200 nm)</td>
</tr>
<tr>
<td></td>
<td>GaAs (100 nm)</td>
<td>Substrate</td>
</tr>
<tr>
<td></td>
<td>Substrate</td>
<td></td>
</tr>
</tbody>
</table>

**Conclusions**

In conclusion, a superfluid cold optics probe has been developed for experiments in semiconductors to temperatures as low as 1.5 K. The system has successfully acquired OPNMR experiments in GaAs. Furthermore, the helicity of the light can be continuously varied from $\sigma^+$ to $\sigma^-$. A Labview automation was developed to automate the acquisition of the OPNMR action spectra and was validated to perform well within the step-size (0.5 nm). Further instrumentation may be needed to re-engineer some aspects of the probe to reach even lower temperatures. Ideally, the probe should be at 200 mK to reach a fully polarized equilibrium state. This may be too low to reach with normal He-4 and may require other equipment such as a He-3 pot to reach such low temperatures.
CHAPTER 4
OPTICALLY ENHANCED NMR OF GALLIUM MANGANESE ARSENIDE

In this chapter, OPNMR in the magnetic semiconductor Ga$_{1-x}$Mn$_x$As is explored. Experiments were performed on thin films of Ga$_{1-x}$Mn$_x$As (where $x=0$, 1 or 0.038) grown by LT-MBE on a bulk crystal of GaAs (635 µm thick). OPNMR experiments were acquired at fields of 3.00 T and 7.05 T at 1.5 K. A light-enhanced NMR signal was observed, but it does not appear to originate from the optical pumping effect as observed in undoped GaAs. We investigated the enhancement and found it to be consistent with a light-induced quadrupolar relaxation mechanism (LIQR). Further experiments were performed on p-type GaAs to investigate if the LIQR mechanism involved acceptor states.

Motivation

In recent years, there has been considerable interest in spin-based electronics or spintronics devices. One approach is to incorporate magnetic impurities into semiconductor materials. Incorporation of Mn into a III-V semiconductor results in a dilute magnetic semiconductor which can exhibit ferromagnetic order at relatively high temperatures. The ferromagnetic order is ideal for magnetic RAM (MRAM) devices that would use spin to encode information. Furthermore, the fact the material is ferromagnetic but still has semiconducting capability makes it readily implementable into everyday machines. Furthermore, Ga$_{1-x}$Mn$_x$As exhibits enhanced spin-orbit coupling due interactions with the d shell electrons. This larger spin-orbit coupling may produce large energy splittings between the heavy hole and light hole in the valence band. If large enough, light could be used to stimulate spin-selective transitions to generate pure electronic spin states, which would be ideal for spintronics applications.
Importantly, to produce high quality GaMnAs films, studies have indicated that the growth temperature be low (200-340 °C) compared to traditional MBE. The solubility of Mn in GaAs is low (roughly $10^{19}$ cm$^{-3}$), therefore, the growth substrate temperature is lowered, which causes non-equilibrium growth conditions. The non-equilibrium conditions increase the Mn content in the epitaxial layer, and thereby circumvents the solubility limitations. Furthermore, low temperature growth can also result in more defects such antisites (e.g. $\text{As}_{\text{Ga}}$) and Mn interstitial sites. Both defects are considered deep defects and can compensate the holes in the film. 

**Light-Induced Quadrupolar Relaxation**

Light-induced quadrupolar relaxation (LIQR) is an interesting phenomenon that is observed in GaAs at laser excitation intensities that are low relative to the intensities required to observe OPNMR signals. Quadrupolar relaxation of nuclear spins is induced via the interaction of the nuclear quadrupole moment with electric field gradients in a material. In materials with a zinc blende crystal structure (e.g. bulk GaAs), the electric field gradient vanishes at the nuclear coordinates, and the interaction is not apparent in the spectra. However, illumination of the sample can lead to fluctuating EFG’s around partially occupied defects in the crystal which causes quadrupolar relaxation of the nuclei. The fluctuations are insensitive to the polarization of the light, and efficiently drive the system to thermal equilibrium. Due to the efficient relaxation, the LIQR effect can lead to quicker nuclear thermalization of the nuclear spin magnetization (i.e. a shorter $T_1$). Paget originally proposed the concept of quadrupolar relaxation in semiconductor materials. Li and co-workers were one of the first research groups to experimentally observe the LIQR effect in the laboratory.
their work, they saw that the LIQR and OPNMR mechanisms both occurred simultaneously, but either could be preferentially selected depending on the optical power. The important parameter in their experiments is the ratio of the two relaxation timescales, \( f \), which was originally modelled by Paget and defined as,

\[
f = \frac{T_Q}{T_H}
\]  

(4-1)

where \( T_Q \) is the quadrupolar relaxation time and \( T_H \) is the hyperfine relaxation time.

These time constants though are not static and depend on the donor occupancy, \( \Gamma \), as well as other parameters. The dependence on \( \Gamma \) for the quadrupolar relaxation rate was derived in Reference 55 as

\[
\frac{1}{T_Q} = 2\Gamma(1-\Gamma)\left(\frac{|e|QR_{14}}{12\hbar}\right)^2\left(\frac{|e|}{4\pi\varepsilon\varepsilon_0}\right)\left(\frac{6}{\omega_N^2\tau_Q}\right)\frac{S^2(r)}{r^4/a_0^4}
\]  

(4-2)

with

\[
S(r) = 1 - \left(1 + \frac{2r}{a_0} + \frac{2r^2}{a_0^2}\right)e^{-2r/a_0}
\]  

(4-3)

where \( |e| \) is the absolute value of the elementary charge, \( \varepsilon \) is the permittivity, \( \varepsilon_0 \) is the vacuum permittivity, \( Q \) is the nuclear quadrupolar moment, \( R_{14} \) is the electrostatic anti-shielding constant, \( \omega_N \) is the nuclear Zeeman frequency, and \( \tau_Q \) is the correlation time of fluctuations of the EFG. The \( S(r) \) term describes the modulation of the electric field, where \( r \) is the distance from the donor and \( a_0 \) is the electronic Bohr radius. The dependence of \( \Gamma \) on the hyperfine rate was derived as

\[
\]  

55
\[
\frac{1}{T_H} = 2\Gamma \left( \frac{|e| QR_{14}}{12 \hbar} \right)^2 \frac{1}{\omega_H^2 \tau_H} e^{\frac{1 - \gamma}{\omega_H}}
\]

(4-4)

where \( \omega_H \) is the frequency associated with the nuclear-electronic “flip-flop”, and \( \tau_H \) is the correlation time of the fluctuations in the hyperfine field. Apparent from Equations 4-2 and 4-4, the LIQR is more efficient relaxation mechanism when \( \Gamma > 0 \) but less than some critical occupancy, \( \Gamma_c \), where the two rates are equal. Beyond \( \Gamma_c \), the hyperfine cross-relaxation would dominate.

Both LIQR and OPNMR lead to larger NMR signals compared to those acquired in the absence of light, but the signal arising from LIQR is still governed by the Boltzmann distribution at thermal equilibrium. Although both the hyperfine cross-relaxation and LIQR are activated by photoexcitation, the underlying difference between the two is LIQR is more effective at low donor occupancy (i.e. low optical intensity), while hyperfine cross-relaxation dominates at high occupancy which occurs at higher optical intensities.\(^{55}\) In previously reported work, the laser intensity dependence of the 71-Ga NMR signal in GaAs reveals two different enhancement regimes which are distinguished by the phase of the NMR signal and its dependence on the optical polarization.\(^{53}\) In the LIQR regime, a positive enhancement is observed independent of the helicity of the light. Conversely, in the hyperfine cross-relaxation regime, the signal is sensitive to the polarization of the light and can give negative/positive enhancements for \( \sigma^+ / \sigma^- \) light.

In Ref 53, the authors suggested that “deep defects” may be responsible for the corresponding LIQR observed in GaAs, in contrast to Paget’s original theory where only shallow donors were responsible. In the original paper by Paget, shallow donors are
responsible for both the quadrupolar relaxation as well as the hyperfine relaxation.\textsuperscript{55} Conversely, deep defects were invoked to rationalize a change in the lineshape of the Ga-71 and Ga-69 NMR signals when transitioning between the OPNMR regime and the LIQR regime by Li and co-workers.\textsuperscript{53, 54} In their work, mechanical strain was induced in the sample via mounting. This strain is observed in the NMR lineshape with the onset of sharp quadrupolar satellites. Under optical pumping conditions, they were able to observe a triplet resulting from the strain. However, under LIQR conditions, they were able to observe only a single peak (i.e. no quadrupolar satellites). They attributed this to the long range quadrupolar interaction, and, in particular, to the deep defects. Deep defects have relatively high electron localization which would result in larger EFG's and an enhanced LIQR.\textsuperscript{53} From the long range LIQR originating from the deep defects, a distribution of different EFG's are probed resulting in extremely broadened satellites which ultimately gave the single line spectrum.

**Experimental Procedures and Sample Preparation**

Three samples were investigated in this work. The first Ga\textsubscript{1-x}Mn\textsubscript{x}As film, which will be referred to as 1\% Mn, was grown via low temperature MBE with a thickness of approximately 800 nm and x= 0.01. The film was deposited on a thin film of AlGaAs (300 nm) on top of a semi-insulating GaAs (001) substrate. The second film, which will be denoted as 3.8\% Mn, was also grown via low temperature MBE with a final thickness of 7 μm and x= .038. This sample was deposited on low temperature GaAs layer (2 nm thick) on top of a semi-insulating GaAs substrate as well. A sample of the semi-insulating GaAs substrate used for growth was compared to the signal as a reference. The 3.8\% Mn sample had a hole density of 10\textsuperscript{20} cm\textsuperscript{-3} and a Curie temperature of
approximately 35 K. The 1% Mn sample remained paramagnetic to 4.2 K and no Curie temperature was recorded.

OPNMR and NMR experiments were conducted in the previously mentioned homebuilt optical NMR probe (Chapter 3) which was inserted into a Janis CDNT-NMR optical cryostat. Experiments were performed at 3.00 T or 7.05 T in two different 89-mm bore Oxford superconducting magnets. Gated light experiments were conducted to investigate the dynamics of the NMR signals. For gating of the laser light, two different methods were used: a Pockel’s cell or a mechanical shutter. For the measurements of the nuclear spin relaxation in the dark, a ConOptics Pockel’s cell (Model 350-50) was mounted in-between two polarizing cube beam splitters with their transmission axes aligned perpendicular to each other. The Pockel’s cell was driven by a ConOptics Model 302 Laser Modulator power supply. When the Pockel’s cell was activated, the polarization axis of the light is rotated by 90°, allowing transmission through the second polarizer. The mechanical shutter was used in the gated power dependence experiments. Both the ConOptics Model 302 driver and the mechanical shutter were controlled via TTL signals from the NMR spectrometer.

**Thermally Polarized NMR of GaAs and GaMnAs at Room Temperature**

Room temperature NMR spectra were acquired of all samples. However, the 1% Mn sample was only 800 nm thick and occupied a miniscule fraction of the coil volume. The poor quality factor with respect to the film and coil, plus the large signal originating from the bulk substrate resulted in a NMR spectrum identical to bulk GaAs. The thermally polarized NMR spectra of the 3.8% Mn sample however was noticeably different. Furthermore, the 3.8% Mn and the bulk GaAs sample were collected at two different magnetic fields: 3.00 T and 7.05 T. The spectra of the two samples at the two
different magnetic fields are presented in Figure 4-1. As depicted, the lineshape of the 3.8% Mn sample at the two different magnetic fields are nearly identical. Since the underlying bulk substrate in this sample is over 90 times thicker than the film, the former is expected to dominate the spectrum. Comparing the linewidths of the bulk GaAs and 3.8% Mn sample at room temperature, significant differences in the linewidth and lineshape can be seen. The 3.8% Mn sample exhibits a broader resonance than bulk GaAs. Furthermore, the linewidth of the Mn doped film is invariant with respect to field strength. Moreover, the effective lineshape changed from a Gaussian in bulk GaAs to a Voigt lineshape (70% Lorentzian, 30% Gaussian by total area under the curve) in the 3.8% Mn sample. This lineshape also appears to be independent of field strength. We attribute the broader component in the 3.8% Mn sample to paramagnetic interactions with the Mn atoms in the film.

Figure 4-1. Thermal Ga-71 NMR spectra at 295 K of bulk GaAs at 3.00 T (black) and at 7.05 T (green), and the 3.8% Mn sample at 3.00 T (red) and 7.05 T (blue). Signals were acquired with 64 scans, 5 s recycle delays, and a 5 μs 90° pulse.
It is important to note that the thermally polarized NMR spectra represent the non-selective detection of all Ga-71 in the entire sample, which is predominantly the GaAs substrate. In contrast, OPNMR can selectively probe the film. OPNMR experiments enhance the nuclear spin polarization near the surface and can therefore selectively sample only the thin film.\textsuperscript{14,56}

Figure 4-2. Representative OPNMR spectra of A) bulk GaAs, B) 1\% Mn and C) 3.8\% Mn using $\sigma^+$ and $\sigma^-$ light, as well as without light (“Dark”). All spectra were recorded with the sequence shown in D). Spectra were collected as a single scan with a 4\us 90° pulse. The sample was irradiated for $\tau_L = 240$ s, with 24 mW (at the sample space) of 1.495 eV light at 1.5 K and 3.00 T.

**Optically Enhanced NMR Spectroscopy of GaAs and GaMnAs**

OPNMR spectra of the bulk GaAs, the 1\% Mn and the 3.8\% Mn samples are shown in Figure 4-2. Bulk GaAs shows a strong negative OPNMR signal when irradiated with $\sigma^+$ polarized light, and a small positive enhancement with $\sigma^-$ light. This
asymmetry of the signal enhancement can be traced to the thermal equilibrium spin polarization of the conduction electrons. In the limit of short irradiation times and neglecting the thermal equilibrium polarization of the nuclei, the OPNMR signal can be described with respect to time, $t$, by

$$I_z \propto \frac{1}{T_1^u} (S_z - S_{eq}) t$$

(4-5)

where $1/T_1^u$ is the cross-relaxation rate, $S_z$ is the expectation value of the conduction electron spin polarization, and $S_{eq}$ is the thermal conduction electron spin polarization.

The conduction electron spin polarization was derived as

$$S_z = \left[ \frac{S_z^0}{1 + \tau e/T_{le}} \right] + \left[ \frac{S_{eq}}{1 + T_{le}/\tau e} \right]$$

(4-6)

where $S_z^0$ is the instantaneous optically induced spin polarization, $\tau e$ is the lifetime of the conduction electron, and $T_{le}$ is the longitudinal spin relaxation time of the conduction electron. For bulk GaAs at 1.5 K and 3 T with $g = -0.44$, $S_{eq} = +0.14$. The expected instantaneous optically induced spin polarization should be $S_z^0 = \pm 0.25$ for $\sigma^-$ light near the band gap (1.519 eV). The small deviation between $\sigma^-$ and thermal equilibrium affords only a modest enhancement, while $\sigma^+$ deviates greatly, and hence produces a very large OPNMR signal.

Interestingly, the acquired signals for the 1% Mn and 3.8% Mn seen in Figure 4-2 sample are vastly different compared to bulk; the signal appears to be positive and practically invariant to the polarization of light. These results are not easily explained in
terms of the simple OPNMR model presented in Equations 4-5 and 4-6. Ideally, when changing the helicity of the light, the value of $S^0_z$ should change. Ultimately, as $S^0_z$ changes, so will $S^z$, and this will be reflected in the deviation away from $S_{eq}$, which is apparent in the OPNMR signal. Despite changing the polarization of the light, the signal appears to be invariant. This can only be explained in the case where $\tau_e > T_{1,e}$ and thus $S^z = S_{eq}$, where cross-relaxation can drive the system to thermal equilibrium. However, the cross-relaxation rate, $1/T_{1''}$, would still be power sensitive as it is directly proportional to $\Gamma$ (see Equations 1-18 and 1-19). In the next section, a power dependence study will investigate this possible effect.

To further investigate the helicity invariance, we acquired action spectra of bulk GaAs, the 1% Mn and the 3.8% Mn samples, shown in Figure 4-3. The OPNMR action spectra for both helicities of the pumping light were acquired. In the case of the bulk GaAs, the measurements agree well with previously observed results for this material.3,12,23 The signal is positive for $\sigma^-$ polarization, negative for $\sigma^+$ polarization, and importantly, the OPNMR signals for a given optical polarization do not change sign (invert) for any photon energy. The oscillations observed in the bulk arise from Landau level quantization of the light hole, heavy hole and conduction bands. Interestingly, the 1% Mn sample appears to possess these oscillations as well. In contrast, the 3.8% Mn action spectra appear nothing like those of the bulk or the 1% Mn sample. The signal remains positive and nearly constant for all photon energies and is essentially invariant to the helicity of the circularly polarized pumping light. Furthermore, the oscillations that are attributed to Landau levels in the bulk sample are not observed in the 3.8% Mn sample.
Figure 4-3. OPNMR action spectra of GaAs (black), 1% Mn (red) and 3.8 % Mn (blue) using $\sigma^+$ and $\sigma^-$ light. All spectra were recorded with the exact sequence shown above in Figure 4-2 under identical conditions (1.5 K and 3.00 T).
Importantly, the 1 % Mn film is only 800 nm thick and is roughly the same thickness as the optical penetration depth of above band gap photons for bulk GaAs. Moreover, from Lambert’s law, the intensity is attenuated by ~36% after 800 nm, implying that 99% of light will be is localized to the top 4 μm. Consequently, the NMR experiment is likely probing both the GaAs support as well as the GaMnAs film. This could possibly explain the matching oscillatory features below 1.51 eV in the action spectra that originate from underlying substrate. We investigated this penetration depth issue via magneto-photoluminescence (MPL). Bulk GaAs fluorescence’s when irradiated with above band gap photons, however, the 1% Mn sample should not, as impurities in the sample quench the fluorescence. The MPL spectrum is exhibited in Figure 4-4 and shows the MPL from 1% Mn sample is identical to bulk GaAs despite the fact no MPL should be observed at all.

![MPL spectra of bulk GaAs (black) and 1% Mn sample (red). Data were acquired with 20 mW of unpolarized 1.520 eV light at 3 T and 1.5 K.](image)
From the results in Figure 4-4, it appears the NMR experiment probes both the film and the substrate. Thus, the data presented in Figure 4-3 may be explained as a superposition of two signals: a signal from the film combined with the OPNMR signal originating from the bulk. The change in sign of the enhancement may result from optical penetration depth effects, in which the light is weakly absorbed by the film and more of the light reaches the substrate. Bulk GaAs has a large negative enhancement below 1.51 eV, and this appears to be replicated by the 1% Mn sample. Furthermore, from the MPL data, we cannot rely on OPNMR to give definitive information from only the film.

Evident in Figure 4-3 is the lack of Landau level oscillations in the 3.8% Mn action spectrum. Although unlikely, the Landau levels may be unresolved due to the field strength. Therefore, the study was replicated for the 3.8% Mn sample at 7.05 T to further increase the separation between different Landau levels. Depicted in Figure 4-5 is the action spectrum at 7.05 T. Noticeably, it is nearly identical to the action spectrum acquired at 3.00 T, except for a small shift in the maximum to higher energy at the higher field. We hypothesize that this maximum may arise from larger penetration depths and hence larger optical excitation volume. Since the band edge is expected to shift to higher energy with increasing magnetic field, the data are consistent with this interpretation. However, the polarization invariance cannot easily be reconciled with the current paradigm of OPNMR as explained in Chapters 1 and 2. We hypothesize that the observed light-induced signal enhancement arises from a LIQR effect.
LIQR effects and Power Dependence of GaAs and GaMnAs

As described earlier, the photoexcited carriers can generate electric fields that fluctuate and couple to the quadrupolar moments of nuclei via the quadrupolar interaction. However, in the absence of light excitation, quadrupolar relaxation is virtually nonexistent at cryogenic temperatures. The quadrupolar relaxation in GaAs is induced by lattice phonons which have negligible concentration at 1.5 K. Furthermore, for semi-insulating GaAs at low temperatures, the $T_i$ is roughly 7 hours at 3 T.6
However, by irradiating the sample at low optical intensity, the LIQR effect can reduce $T_1$ and effectively enhance the NMR spectrum. Moreover, the lack of photon polarization dependence is consistent with the work of Li et al.\textsuperscript{54} In the case of GaMnAs films, all the data were collected in the high power regime, where in GaAs, the hyperfine cross-relaxation is the dominant enhancement mechanism. The lack of an OPNMR signal may suggest that optical dynamic nuclear polarization does not occur in the GaMnAs. There are many reasons this may be so, such as a reduction of the $T_{1,e}$. Alternatively, it may be LIQR is more efficient. In the model proposed in Ref. 53, two types of defects are postulated: deep and shallow defects, which are assigned to the LIQR and hyperfine-dominated relaxation, respectively. In the growth process of GaMnAs, the low temperature MBE process is prone to include these deep defects (i.e. antisites and interstitial Mn centers). Due to the growth process, there may be an abundance of these deep defects which may allow for a more abundant LIQR to occur.

Figure 4-6 presents the dependence of the Ga-71 NMR signals of the bulk GaAs, 1\% Mn, and 3.8\% Mn samples recorded as a function of the laser irradiation power for $\sigma^+$ polarization. The trend in the data for bulk GaAs agrees well with the data reported in the literature for a similar sample.\textsuperscript{53, 54} After passing through a small positive maximum, the signal decreases and then changes sign. The negative signal decreases linearly above \textasciitilde5 mW. According to the explanation in the literature, the NMR signal is dominated by the contribution induced by electron-nuclear hyperfine cross-relaxation at relatively high laser power.\textsuperscript{53}
The optical power dependence of the NMR signal for the 3.8 % Mn sample (blue), and GaAs (black) at 1.5 K and 3 T. The spectra were collected with 120s of 1.5015 eV light, with $\sigma^+$ polarization.

The 3.8% Mn sample exhibits a similar trend at very low power but shows a completely different behavior at higher powers. The signal increases, saturates to a positive value at very low power (~5 mW), and then becomes independent of power, never decreasing or inverting. According to Paget, in bulk GaAs the LIQR effect should diminish as the power increases above some critical value. Paget explains that as the donor occupancy approaches unity, the EFG is no longer modulated and the
quadrupolar relaxation is eliminated. According to the model, the optical power corresponding to an occupancy of $\Gamma = 0.5$ is\textsuperscript{55}

$$P_0 = L\hbar v k N_A N_D,$$

where $L$ is the electron diffusion length, $\hbar \nu$ is the photon energy, $k$ is the bimolecular recombination coefficient, and $N_i$ is the concentration of the acceptors ($i = A$) and the donors ($i = D$). For the specific case of the power dependence experiments in the 3.8\% Mn sample, $L \sim 160$ nm,\textsuperscript{42} $k \sim 10^{-15}$ m$^3$ s$^{-1}$,\textsuperscript{38} $N_D = 1 \times 10^{22}$ m$^{-3}$,\textsuperscript{55} and measurements show $N_A = 1 \times 10^{26}$ m$^{-3}$. This would correspond to $P_0 = 4.4$ kW, indicating that our experiments were conducted well below $\Gamma = 0.5$, and therefore still in the LIQR regime.

Lastly, the 1\% Mn sample reveals a dependence comparable to bulk GaAs. Again, the film is semi-transparent as discussed earlier, but an important feature is observed in the power dependence. The maximum is larger in the 1\% Mn sample than the 3.8\% Mn which may mean that LIQR is occurring in the film and the substrate and not just the substrate.

Interestingly, for the 3.8\% Mn sample, the LIQR seems to saturate in the high-power regime. This saturation has never been observed before because in the high-power regime, typically hyperfine cross-relaxation dominates and the LIQR signal is not noticeable. However, the apparent saturation may indicate that the relaxation mechanism may be very fast (faster the 240 s used in the experiment), and that the film rapidly reaches thermal equilibrium, even at low powers. We investigated the dynamics of the LIQR signal in the 3.8\% Mn sample by using a standard saturation-recovery sequence and measured the LIQR signal as a function of the delay time. Depicted in
Figure 4-7 is the saturation-recovery data using two different photon energies. The curves in Figure 4-7 reveal that the saturation in the power dependence does not occur due to rapid thermalization of the film as the signal continues to grow with longer delays. The power dependence experiments used 240 s of optical irradiation, and from the data, the apparent time constant is much larger than 240s. Therefore, the saturation must originate from another mechanism. Interestingly, it appears that the time constant for the LIQR signal is photon energy dependent. It may occur due to different penetration depth effects as 1.512 eV is below the nominal band gap of bulk GaAs.

![NMR spectra and saturation-recovery data](image)

Figure 4-7. NMR spectra of the 3.8% Mn sample using various delays and two different photon energies. Spectra on the left were integrated and plotted as a function of time to the right.

Li et al. investigated the effects of nuclear spin diffusion and proposed that the LIQR signal enhancement was ‘bottlenecked’ due to the low content of spin diffusion in the strong EFG surrounding the deep defect. To test this hypothesis, experiments with gated light were performed, where the light was shuttered off for a variable period to
allow more time for spin diffusion to occur. The spin diffusion bottleneck could explain the observed saturation of the NMR signal with respect to the laser power as spin diffusion becomes the rate-limiting process for the growth of the LIQR-induced NMR signal. In the experiment, the shutter was open for 50 ms and then closed for 250 ms, and the cycle was repeated 4800 times for a total irradiation time of 240 s. The gated power dependence is reported in Figure 4-8. In contrast to the results presented in Figure 4-6, where the signal plateaus at a laser power of about 5 mW, LIQR-induced signal saturates at 30 mW when a dark period is incorporated into the cycle. Therefore, the results confirm that the plateau in the power dependence of the NMR signal under continuous irradiation is due to a spin diffusion bottleneck.

![Figure 4-8](image.png)

**Figure 4-8.** Left: NMR spectra acquired at various laser powers when the illumination time of 50 ms was interleaved with 250 ms with no illumination. The laser on-off cycle was repeated 4800 times for a total irradiation of 240 s. Right: NMR peak integrals are plotted with respect to the laser power. All spectra were acquired as 1 scan with a 5 μs pulse at 3 T and 1.5 K. The photon energy was 1.540 eV with \( \sigma^+ \) polarization.
LIQR and Nuclear Spin Polarization Diffusion Study

Based on the understanding that the light-induced NMR signals observed in GaMnAs are sensitive to dark periods, the dynamics were probed in another variation of the gated light experiment. An illumination period of 2.5 ms was followed by a variable dark interval, and the laser on/off cycle was repeated 12000 times to yield a total illumination time of 30 s. By varying the length of the dark interval, the nuclear spin diffusion was probed. According to Li et al., nuclear spin diffusion is active during both the light and dark intervals. When illuminated, nuclei near the defect center are rapidly relaxed to the thermal equilibrium spin polarization. During the dark interval, spin diffusion depolarizes the nuclei near the defect, while the spin polarization diffuses out into the bulk crystal. Upon illuminating again, the nuclei proximal to the defect may be re-polarized via LIQR. In the pulse sequence shown in Figure 4-9, the nuclear spin polarization in the crystal is initially saturated via a train of 90° pulses. After illumination, a gradient is established in the polarization around the deep defect which leads to the diffusion of the spin polarization outward into the bulk. Therefore, if the light is gated with alternating periods of light and dark, in a polarize-diffuse-polarize loop, the polarization of nuclei via the LIQR effect can be extended to a larger volume of nuclei that can give rise to larger NMR signals. Furthermore, because the total time increases in these experiments, the data were collected with light on and light off to subtract the thermal background signal. The data plotted in Figure 4-9 were normalized to their maximum value for each trace. The fact that the signal grows with increasing $\tau_D$ suggests that the observed signals in the Mn-doped signal originate from a LIQR
mechanism where the polarization induced during illumination is given time to diffuse away from defect centers.

![Diagram of pulse sequence](image)

Figure 4-9. The diffusion study in the shuttered LIQR experiment using the pulse sequence shown above. The laser was gated on for $\tau_L$ (2.5 ms) and off for $\tau_D$. The on-off cycles were repeated 12000 times to have the total time of irradiation equal to 30 s for all experiments. The NMR signal for the 3.8 % Mn sample (red) and GaAs (black) are shown. The spectra were collected with 24 mW of 1.5015 eV light, with $\sigma^+$ polarization, at 3 T and 1.5 K. Both data sets were normalized to their maximal value.
The experiments on the GaMnAs films indicate that OPNMR is ineffective in these samples at all laser intensities, and that only the LIQR is effective. A possible explanation for these observations involves the role of Mn as an acceptor in this material: it is a p-type dopant, which has the effect of pushing the chemical potential below the top of the valence band. Kotur and coworkers recently investigated quadrupolar relaxation in p-type GaAs via optically detected nuclear magnetic resonance at low magnetic fields and observed a short nuclear spin $T_1$ (approximately 100 ms at 10 K and from 5-100 G).\textsuperscript{59} They attributed the rapid relaxation to quadrupolar relaxation facilitated by the fluctuating electric field of charged acceptors near donors. However, this relaxation mechanism occurred in the dark. Since no measurements were performed at high magnetic fields, we attempted to observe LIQR and/or OPNMR in p-type GaAs (Wafer Technology Ltd., Ingot no. WV 20940/Zn, Carrier concentration: $3.1E19 \text{ cm}^{-3}$, Mobility: 93 cm$^2$ V$^{-1}$ s$^{-1}$). OPNMR signals could not be observed for the p-type GaAs, and no LIQR-induced signals could be detected. Importantly, the OPNMR/LIQR experiments were performed were much longer than 100 ms (the measured $T_1$ at low field). Consequently, it was possible the system rapidly thermalized without the need of the light source. To ensure that the system was not rapidly relaxing in the dark, we measured the dark $T_1$ using a standard saturation-recovery pulse sequence. We found the $T_1$ to be 36 min at 3 T and 1.5 K. Our experiments are only minutes long, and therefore, the results indicate that the rapid spin lattice relaxation mechanism that takes place in p-type GaAs is not responsible for the LIQR effect observed in the 3.8% Mn sample. Furthermore, for a thorough investigation, we attempted to observe OPNMR/LIQR in n-type GaAs (Wafer
Technology Ltd., Ingot no. WV 22218/Si, Carrier concentration: 1.8E19 cm⁻³, Mobility: 2940 cm² V⁻¹ s⁻¹) and saw no evidence of either enhancement as well.

Currently, the exact reason responsible for the LIQR enhancement is unclear. Addition of Mn could possibly shorten the \( T_{i,e} \) (the electronic spin lattice relaxation time) considerably. If the \( T_{i,e} \) is on the order of the lifetime of the exciton or shorter, the conduction electrons will thermalize and no OPNMR would occur, however the quadrupolar relaxation mechanism would be unaffected. Furthermore, the LT-MBE growth process is known to included deep defects. The increased concentration of deep defects could also be responsible for the LIQR enhancement observed. Clearly, further work needs to be done to explain all our data.

**Conclusions**

To summarize, we have completed the first investigation of Ga\(_{1-x}\)Mn\(_x\)As (\( x = 0.01, \) and 0.038) under conditions of low temperature an optical irradiation and compared the results to the undoped bulk GaAs. Action spectra of the 1% Mn film and 3.8% Mn film revealed that the optically-induced signal is insensitive to the polarization of the incident light with an almost constant enhancement throughout the entire photon energy range, consistent with a LIQR mechanism. A power dependence study showed that the LIQR mechanism is efficient in thermalizing the nuclear spin polarization in both GaAs and GaMnAs at low optical power. However, at higher light intensities, the behavior of the samples diverge. In the 3.8% Mn film, the signal saturates to a positive value at high optical power, while in the bulk GaAs, hyperfine cross-relaxation becomes effective and the signal inverts and increases in proportion to the light intensity (for sufficiently short pumping times). The saturation in the power dependence was investigated using a
gated light experiment, which suggest that the LIQR is diffusion limited. Lastly, the
dynamic studies were conducted via a gated light experiment with variable dark times to
compare the processes of nuclear spin diffusion. We attempted to assign the
effectiveness of the LIQR mechanism to the abundance of electrical acceptors by
investigating p-type GaAs. However, the, p-type GaAs sample yielded no OPNMR or
LIQR-induced signals. Further work is needed to investigate the lack of OPNMR signal
in the Mn-doped film and clarify the details of the light-induced relaxation.
CHAPTER 5
OPNMR STUDY OF STRAIN RELAXATION IN GALLIUM ARSENIDE/SAPPHIRE
BILAYER COMPOSITES

This chapter presents the application of OPNMR to the study of mechanical strain and strain relaxation effects in GaAs/Sapphire bilayers. A single crystal of GaAs (363 μm thick) was epoxy-bonded to a Sapphire support wafer (600 μm thick), and then the GaAs was thinned using a wet chemical etchant. A series of such bilayer structures were prepared with GaAs thicknesses ranging from 363 μm to 80 μm. After curing the epoxy bond at 353 K, the samples were then cooled to 1.5 K, thus inducing strain via differential thermal contraction. The strain in the GaAs layer was observed via measurement of the Ga-71 quadrupole splitting in the OPNMR spectrum acquired at 1.5 K. From the known relationship between the electric field gradient and elastic strain tensors, the quadrupole splitting can be used to estimate the strain in the material localized to the volume detected by OPNMR. Spectra were collected and the quadrupolar splitting was measured as a function of the GaAs layer thickness. The strain relaxation mechanism in the GaAs/Sapp composite was found to be consistent with a mechanical bowing response.

Motivation

Lattice strain has been harnessed in recent years to improve device performance. For example, strained field effect transistors demonstrate increased mobility and increased current gain. Strain has also been utilized to vary the operating wavelength of a solid state laser. Strain lifts degeneracies within the valence band and can be useful as a tool for spintronics applications or even quantum computing. Multiple techniques have been developed to measure microscopic strain in crystalline solids: scanning electron microscopy (SEM), transmission electron microscopy
(TEM)\textsuperscript{63} and X-ray diffraction (XRD)\textsuperscript{64}. However, SEM and TEM characterize the strain indirectly by the statistics of dislocation densities. XRD does probe strain directly but requires advanced instrumentation and techniques.

We recently investigated strain in GaAs/Si bilayers prepared by epoxy-bonding a GaAs wafer to a Si wafer.\textsuperscript{56} Upon cooling the samples to temperatures below 10 K, strain was induced due to differential thermal contraction of the two materials, resulting in a quadrupolar splitting of the Ga-71 OPNMR line. By measuring the strain for a series of samples with different layer thicknesses, we were able to confirm the dominant elastic strain relaxation mechanism was a mechanical bowing response, which is dependent on the relative thicknesses of the two layers.\textsuperscript{65} In this chapter, we adopt a similar experimental approach to investigate the strain in GaAs/sapphire (GaAs/Sapp) bilayer composite samples. OPNMR spectra were collected to probe the local strain in the GaAs/Sapp composite at cryogenic temperatures. As in the previous study using the Si support, a series of composites were prepared where the GaAs was selectively thinned to evaluate the mechanical bowing response in this system. This chapter will first review how strain is detected in the NMR spectrum, and then how OPNMR can measure the local strain. Lastly, we will discuss the mechanical bowing model presented by Wood et al. and show how this model can be adapted to the present application to the GaAs/Sapp composites.\textsuperscript{56}

\textbf{Strain and NMR}

NMR of quadrupolar nuclei can report on the local strain in various materials via distortions in the electric field at the nuclear coordinates.\textsuperscript{47,66-69} Although the chemical shift anisotropy is also sensitive to strain,\textsuperscript{66} the method employed in this work focuses on the changes in the quadrupolar coupling constant. In crystalline materials, where the
lattice is cubic, the electric field gradient (EFG) vanishes at the nuclear sites. The absence of an EFG results in a single line NMR spectrum. The EFG can be re-induced using strain or other means to lower the lattice symmetry. In our experiments, GaAs was epoxy bonded to crystalline sapphire at 353 K, and then cooled to 1.5 K to induce a biaxial strain via differential thermal contraction. Here we will review how the EFG and ultimately the strain in the sample can be deduced from the experimentally observed quadrupolar splitting.\(^{56}\) According to Equation 1-9, the \(V_{zz}\) component of the EFG tensor (in the principle axis system) is expressed in terms of the quadrupolar splitting \(\Delta \nu_q\) as

\[
V_{zz} = \frac{2h}{eQ} \Delta \nu_q
\]

(5-1)

where \(e\) is the elementary charge, \(h\) is Planck’s constant, \(Q\) is the nuclear quadrupolar moment and \(\Delta \nu_q\) is in units of Hz. The elements of the EFG are related to elastic strain \(\varepsilon\) by the gradient-elastic tensor \(S_{ijkl}\).\(^{70}\)

\[
V_{ij} = \sum_{kl} S_{ijkl} \varepsilon_{kl}.
\]

(5-2)

Strains where \(k \neq l\) are not considered in this case. As noted in Chapter 2, the cubic symmetry of GaAs reduces the number of unique values, and thus Equation 5-2 can be reduced to\(^{35}\)

\[
\begin{bmatrix}
V_{xx} \\
V_{yy} \\
V_{zz}
\end{bmatrix} =
\begin{bmatrix}
S_{11} & S_{12} & S_{12} \\
S_{12} & S_{11} & S_{12} \\
S_{12} & S_{12} & S_{11}
\end{bmatrix}
\begin{bmatrix}
\varepsilon_{xx} \\
\varepsilon_{yy} \\
\varepsilon_{zz}
\end{bmatrix}
\]

(5-3)

where the element \(V_{zz}\) is defined as,
\[ V_{zz} = S'_{12} \varepsilon_{xx} + S'_{11} \varepsilon_{zz} \] (5-4)

As previously mentioned, when the sample is cooled down, differential thermal contraction produces a biaxial strain where \( \varepsilon_{xx} = \varepsilon_{yy} \). Equation 5-4 reduces to

\[ V_{zz} = 2 S'_{12} \varepsilon_{xx} + S'_{11} \varepsilon_{zz} \] (5-5)

Using the relationship \( 2 S'_{12} = -S'_{11} \), Equation 5-5 simplifies to\(^{70}\)

\[ V_{zz} = -S'_{11} \varepsilon_{xx} + S'_{11} \varepsilon_{zz} \] (5-6)

The compliance tensor, \( S_{ij} \), relates the strains along the x and z axes. Cubic crystal structures can be treated as isotropic materials, and therefore, \( \varepsilon_{kl} = 0 \) for \( k \neq l \), and

\[
\begin{bmatrix}
\varepsilon_{xx} \\
\varepsilon_{yy} \\
\varepsilon_{zz}
\end{bmatrix} = 
\begin{bmatrix}
S_{11} & S_{12} & S_{12} \\
S_{12} & S_{11} & S_{12} \\
S_{12} & S_{12} & S_{11}
\end{bmatrix}
\begin{bmatrix}
\sigma_{xx} \\
\sigma_{yy} \\
\sigma_{zz}
\end{bmatrix}. \] (5-7)

In our experimental arrangement, equal stresses were applied in the x and y directions (and none along the z). Therefore, Equation 5-7 simplifies to (previously derived in Chapter 2):

\[ \varepsilon_{xx} = \varepsilon_{yy} = S_{11} \sigma + S_{12} \sigma \] (5-8)

and,

\[ \varepsilon_{zz} = 2 S_{12} \sigma. \] (5-9)

From Equations 5-8 and 5-9, \( \varepsilon_{zz} \) can be related to \( \varepsilon_{xx} \) which can be used to reduce Equation 5-6,

\[
V_{zz} = -S'_{11} \frac{S_{11} + S_{12}}{2S'_{12}} \varepsilon_{zz} + S'_{11} \varepsilon_{zz}. \] (5-10)
Finally, Equation 5-10 is combined with Equation 5-1 to relate the strain to the quadrupolar splitting:

$$|\varepsilon_{zz}| = \frac{2h}{eQ} \left( 1 - \frac{S_{11} + S_{12}}{2S_{12}} \right)^{-1} \frac{1}{S_{11}} \Delta v_Q$$

(5-11)

Note that the absolute value of the strain is related to the quadrupolar splitting since the NMR experiment is insensitive to the sign of the EFG. Using the numerical values for the material parameters and the $^{71}\text{Ga}$ nuclear quadrupole moment, $Q$, provided in Table 5-1 we can deduce the strain from the observed quadrupolar splitting as:

$$|\varepsilon_{zz}| = \frac{1.38 \times 10^{-5}}{\text{kHz}} \Delta v_Q$$

(5-12)

Table 5-1. Material parameters for GaAs

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
<th>Reference</th>
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<tbody>
<tr>
<td>$Q$</td>
<td>$1.07 \times 10^{-25}$ (for Ga-71)</td>
<td>cm$^2$</td>
<td>$^{71}$</td>
</tr>
<tr>
<td>$S_{11}$</td>
<td>$1.17 \times 10^{-12}$</td>
<td>cm$^2$ dyn$^{-1}$</td>
<td>$^{72}$</td>
</tr>
<tr>
<td>$S_{12}$</td>
<td>$-0.37 \times 10^{-12}$</td>
<td>cm$^2$ dyn$^{-1}$</td>
<td>$^{72}$</td>
</tr>
<tr>
<td>$S'_{11}$</td>
<td>$-9.1 \times 10^{-15}$</td>
<td>statC cm$^{-3}$</td>
<td>$^{73}$</td>
</tr>
</tbody>
</table>

**Sample Preparation**

The GaAs/Sapp composite samples were prepared from as-received single crystal wafers. The GaAs was cleaved from a 363 ± 25 μm thick semi-insulating GaAs wafer from Wafer Technology LTD (ingot no. M2/835/Un). The sapphire was cleaved from a 600 μm thick wafer from University Wafer (ID no. 2561). The $\langle 100 \rangle$ plane of the
GaAs was epoxied to the \( \{0001\} \) plane (c-plane) of the sapphire, with the \( \{010\} \) approximately parallel to the sapphire’s \( \{00\overline{1}0\} \) plane (m-plane). The epoxy was Stycast 1266, which was cured at 353 K for 12 hours. Two other identical samples were prepared and subsequently etched in a \( \text{H}_2\text{SO}_4/\text{H}_2\text{O}_2/\text{H}_2\text{O} \) (1:8:1 by volume) solution. Trial runs revealed that there was no loss of sapphire or epoxy after 6 hours immersed in the etchant. After etching, the final GaAs thicknesses were 80 and 180 µm, measured using a precision mechanical micrometer.

**NMR and OPNMR of GaAs/Sapphire Composites**

Room temperature (thermally polarized) Ga-71 NMR spectra were acquired on the GaAs/Sapphire (GaAs/Sapp) composites on a Tecmag Scout™ spectrometer. All spectra were acquired under identical conditions with 5 µs 90° pulse, 5 s recycle delay, and 64 scans. The lineshape did not change significantly with decreasing GaAs thickness and no quadrupolar splitting was evident in the room temperature thermally polarized spectra, which are presented in Figure 5-1.

OPNMR spectra of the same set of samples is presented in Figure 5-2. As evident in the spectra, the quadrupolar splittings and hence the strains vary drastically with GaAs layer thickness. The strain is induced by the mismatch in the rates of thermal contraction when the sample is cooled from room temperature to 1.5 K where the OPNMR spectra are acquired.\(^74\) For example, the unetched sample has a quadrupole splitting of 4.2 kHz at cryogenic conditions, but the splitting was unresolved at room temperature.
Figure 5-1. Thermally polarized NMR spectra of a series of GaAs/Si composites at room temperature (295 K and 3.00 T). Spectra were acquired using 5 μs 90°-pulses, with 64 scans and 5s recycle delay.

It is important to note that the thermally polarized room temperature NMR signals originate from the entire volume of the GaAs layer whereas the OPNMR is selective to nuclei located close to sample surface, depending on the photon energy. In the case of photons above the band gap (1.519 eV), the optical absorption length is limited to approximately 800 nm from the surface. From the work of Kuhns and coworkers, nuclei far removed from the surface can also be hyperpolarized due to nuclear spin diffusion. For the pumping times used in the experimental protocol (480 s) used here, the nuclear spin diffusion is estimated to be approximately 120 nm ($D \approx 30 \text{ nm}^2\text{s}^{-1}$).

Furthermore, the conduction electron can also diffuse as well. Two time-scales are important to consider for this diffusion: the conduction electron spin relaxation time and the free exciton recombination lifetime. In the case of semi-insulating GaAs at cryogenic temperatures and high field, the free exciton lifetime becomes the limiting
time constant. The electronic spin diffusion length in one-dimension, $l_e$, is calculated using

$$l_e = \sqrt{D\tau}$$

where $\tau$ is the free exciton lifetime and $D$ is the ambipolar diffusion constant. From the literature, $D = 170 \text{ cm}^2\text{s}^{-1}$ and $\tau = 1.07 \text{ ns}$ and consequently, $l_e \approx 4.3 \text{ µm.}$

Considering the contributions of the nuclear and electronic spin diffusion and the optical penetration depth, the OPNMR detection is selective to the top 5.2-8.4 µm of the sample for excitation with photons above the band gap.

![Surface and Interface OPNMR Spectra](image)

Figure 5-2. OPNMR spectra of the same series depicted in Figure 5-1. Spectra were collected at 1.5 K with 200 mW of $\sigma^+$ light (1.519 eV), using a 4 µs 90°-pulse, and 8 minutes of optical pumping time. Furthermore, spectra were collected at the sample surface (black) and at the GaAs/Sapp interface (red).

Given the inherently small volume that OPNMR spectroscopy probes, OPNMR spectra can quantify the local strain near the irradiated surface of the GaAs layer. As seen in Figure 5-2, the magnitude of the quadrupolar splitting increases from 4.2 kHz
µm to 17.6 kHz as the GaAs is thinned from 363 µm down to 80 µm at the surface. Clearly, the extent of the strain relaxation, as measured at the outer surface of the GaAs layer, depends on its thickness relative to that of the support. According to the mechanical bowing model proposed by Wood et al., the mismatch between layers is largest near the interface of the two materials and therefore, so is the strain, while the strain is reduced at the opposite surface due to the mechanically induced curvature (i.e. bowing) of the composite. Fortunately, sapphire and Stycast 1266 are both transparent in the NIR regime which allows for direct OPNMR measurements of the strain at the interface. Therefore, we also measured the interfacial strain of the exact same samples. From Figure 5-2 we see the interfacial strain is larger than the surface strain and increases with decreasing GaAs thickness. To explain this increase, we invoke the mechanical bowing strain relaxation model adapted to the GaAs/Sapp bilayer system in the next section.

**Bowing Strain Relaxation Model**

We modelled the strain relaxation in the composite using a mechanical bending or “bowing” model. The model is adapted from Wood et al. and is based on the general multilayer formalism of Townsend and collaborators. In this model, the elastic moduli of both the substrate and the film are considered, as well as their respective thicknesses. Furthermore, the model contains no free/fitted parameters.

In the model, the GaAs and sapphire layers, with lengths $d_i$, are initially unbonded. Next, the samples are deformed with two axial end forces, such that each layer of the composite has the same length $d_0$. The deformation results in an elastic strain $\varepsilon_{i,0}$ in each layer. This strain alone does not satisfy the requirement of zero...
resultant axial forces at static equilibrium, and therefore an additional strain, $\varepsilon_{i,F}$, is introduced so that the sum of the axial forces is zero. Lastly, when the axial forces are removed and the layers are bonded, the composite will bow, which introduces a bending strain element, $\varepsilon_{i,M}$. The resulting strain throughout the material is therefore

$$\varepsilon_i = \varepsilon_{i,0} + \varepsilon_{i,F} + \varepsilon_{i,M}.$$  (5-14)

According to Townsend,\textsuperscript{65}

$$\varepsilon_i = \ln \left( \frac{1}{d_i} \right) + \sum_j E_j t_j \ln (d_j) \sum_j E_j t_j + (\pi - z) K$$  (5-15)

where $E_j$ is the elastic modulus and $t_j$ is the thickness of the $j^{th}$ layer, $\pi$ is the position of the neutral plane, $z$ is the distance of the plane normal to the linear dimension of the sample, and $K$ is the curvature of the composite. The neutral plane is the plane along the $z$ dimension in the composite where the total internal forces disappear. The solution to finding the location of the neutral plane in the composite is\textsuperscript{65}

$$\pi = \frac{t}{2} \left( \sum_i E_i \gamma_i \frac{t_i}{2} / \sum_i E_i t_i \right)$$  (5-16)

where $\gamma_i$ is effectively a placeholder in the composite: $\gamma_1 = t_{GaAs}$ and $\gamma_2 = -t_{Sapphire}$.\textsuperscript{56} The curvature of the composite is given by\textsuperscript{65}

$$K = \frac{\sum_i E_i \gamma_i \frac{t_i}{2} \left[ -\ln(d_i) + \sum_j E_j t_j \ln(d_j) / \sum_j E_j t_j \right]}{\sum_i E_i t_i \left[ \frac{\pi t}{2} - \frac{t^2}{3} + \frac{\gamma_i}{2} (t - \pi) - \frac{3\gamma_i^2 + t_i^2 - t^2}{12} \right]}. \quad (5-17)$$
Lastly, for all materials and geometries in the composites, the elastic moduli are the biaxial elastic moduli. The biaxial elastic modulus is derived from the linear elastic modulus by $E_j = E_j^{\text{linear}} \sqrt{(1 - \nu_j)}$ where $\nu_j$ is the Poisson ratio. The Poisson ratio is defined as the ratio of the compliance tensor components:

$$\nu_j = -\frac{S_{12,j}}{S_{11,j}}. \quad (5-18)$$

The material parameters needed to solve Equation 5-17 are given in Table 5-2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>$E_{\text{GaAs}}$</td>
<td>87.88</td>
<td>GPa</td>
<td>72</td>
</tr>
<tr>
<td>$E_{\text{Sapphire}}$</td>
<td>464</td>
<td>GPa</td>
<td>78</td>
</tr>
<tr>
<td>$S_{11,\text{GaAs}}$</td>
<td>1.17 E -12</td>
<td>cm$^2$ dyn$^{-1}$</td>
<td>72</td>
</tr>
<tr>
<td>$S_{12,\text{GaAs}}$</td>
<td>-0.37 E -12</td>
<td>cm$^2$ dyn$^{-1}$</td>
<td>72</td>
</tr>
<tr>
<td>$S_{11,\text{Sapphire}}$</td>
<td>2.326 E -12</td>
<td>cm$^2$ dyn$^{-1}$</td>
<td>78</td>
</tr>
<tr>
<td>$S_{12,\text{Sapphire}}$</td>
<td>-0.6938 E -12</td>
<td>cm$^2$ dyn$^{-1}$</td>
<td>78</td>
</tr>
</tbody>
</table>

In summary, the predicted strain by the mechanical bowing model is explicitly dependent upon the materials elastic moduli, Poisson ratios, and importantly, their relative thicknesses. Furthermore, the model has no unknown parameters. The strain is directly proportional to the quadrupolar splitting, and therefore, the expected splitting from Equation 5-17 is plotted for variable thicknesses of GaAs on a 600 μm thick sapphire substrate (black trace) in Figure 5-3.
As observed in Figure 5-3, the interfacial strain is plotted along with the surface strain. From the experimentally acquired data, we observe that the interfacial strain increases from 11.5 kHz to 17.6 kHz with decreasing GaAs thickness using the exact same experimental parameters for the surface measurements. Interestingly, the theory predicts that strain at the surface will approach the strain at the surface at thinner GaAs thicknesses. This arises from the inability of the GaAs layer to overcome the rigidity of the much thicker sapphire support, and results in no curvature. Our experimentally acquired splitting appears to agree with the theory, as the 80 μm sample has the same splitting at the interface and surface.

In Figures 5-2 and 5-3, the experimentally observed interfacial splitting is significantly larger than the splitting predicted by the model for all samples. The quadrupolar splittings observed for the samples were approximately 2.5 kHz larger than expected. This may be due to the deformations in the epoxy layer which is not considered in modelling of the composite. Ideally, the epoxy is considered as a lossless bond, but from our data, especially at the interface, it appears it is not lossless. However, compared to previous data acquired in GaAs/Si composites, the overall deviation from theory is much smaller (2.5 kHz compared to approximately 8 kHz).

The results demonstrate that the surface strain and interfacial strain dependence on the GaAs thickness are accurately described by the bowing strain relaxation model. Furthermore, the observation that the two different strains approach each other at thin GaAs thicknesses further validates the model. However, the model does not take into consideration the epoxy layer which transfers the stress from the substrate to the sample itself. Ideally, the theory could be modified to include the epoxy layer as its own
independent layer. Furthermore, it is important to note that strain relaxation can originate from other relaxation schemes as well (e.g. dislocation generation), but for reasons discussed in Ref. 54, the bowing model appears to be the consistent with the observed strain relaxation in this system.

![Figure 5-3](image)

**Conclusion**

We have shown that the quadrupolar splitting can be used an effective tool to quantify strain as well as to investigate the strain relaxation mechanism in a material. Epoxying GaAs to a Sapphire substrate at 353 K and cooling the samples to room temperature induced a biaxial tensile strain in the GaAs which was undetectable in the thermally polarized NMR spectrum. Upon cooling the sample to cryogenic temperatures, the strain increased with their different contraction rates and resulted in even larger quadrupolar splittings. OPNMR spectra were acquired at the nominal band...
gap of GaAs to measure the local strain at the surface and interface of the GaAs. The strain relaxation mechanism was investigated by acquiring spectra on a series of samples with varied GaAs thicknesses. The results qualitatively agreed with a mechanical bowing of the composite. The interfacial strain dependence on the thickness of the GaAs the data was reproduced by the bending model.
In this chapter, the approach developed in Chapter 5 is expanded to the investigation of the photon energy dependence of the OPNMR signal in the GaAs/Sapp composite. The advantage of sapphire is its transparency in the NIR regime, which affords OPNMR spectroscopy to selectively detect a thin layer at the buried GaAs/Sapp interface in addition to selectively detecting the outer surface of the GaAs, all in one sample. The goal is to obtain a more complete understanding of the strain relaxation and to validate the mathematical model for the elastic interaction in the bilayer composite. The Ga-71 OPNMR action spectrum of the bilayer sample was acquired, and a strain-induced inversion of the OPNMR signal was observed for both the surface and the interface. Although it was theoretically predicted, no one to date has reported an inversion in the OPNMR action spectra in bulk GaAs, inversions in the OPNMR signal in bulk GaAs have not been previously reported, even when strained.\textsuperscript{47, 79} The OPNMR signal inversion is attributed to valence band splitting, allowing for spin-selective optical pumping. Lastly, we also show that the quadrupolar splitting can be used to indirectly infer the absorption spectrum. We model the absorption spectrum and then validate our results with simulations of the OPNMR lineshape.

**Motivation**

The work presented in Chapter 5 focused on the application of OPNMR to quantify strain. Investigation of strain at buried interfaces using OPNMR was the subject of two recent studies.\textsuperscript{79, 80} In both reports, the quadrupolar splitting changed as a function of photon energy. The change was attributed to the varying optical
penetration depths and the strain gradient. When irradiating at energies below the band
gap, photons penetrate further into the sample, thereby probing a distribution of strains.
This distribution would lead to a broadening effect and some apparent splitting that
depends on the strain gradient and the optical penetration profile. When irradiating with
at energies above the bandgap, the light is entirely absorbed within 5 μm of the surface
(see Chapter 5). The smaller volume of detection will probe a smaller distribution of
strains, leading to a different quadrupolar splitting. However, the quadrupolar splitting
observed in previous works was either very broad and suffered from weak intensity or
was unresolved from the central transition. Furthermore, neither of the two previous
studies attempted to quantitatively model the underlying strain relaxation mechanism.
Our previous work in Chapter 5 suggests that strain relaxation mechanism is consistent
with a mechanical bowing model. Consequently, because we know how the strain
relaxes through the material, we should be able to assign spatial information about the
observed quadrupolar splitting.

Furthermore, the applied strain can induce valence band splitting that can be
exploited to overcome the fundamental limit on the conduction electron spin polarization
in GaAs. Recall from Chapter 2 that in unstrained GaAs, the light hole and heavy hole
bands are nearly degenerate. Consequently, with strain, optical pumping can overcome
the 50 % polarization limit that is imposed by the optical selection rules. The work
described in this chapter shows that for larger values of strain it is possible to split the
light hole and heavy hole bands to increase the optically induced electron spin
polarization.
Experimental Procedures

Samples were described in the Sample Preparation section of Chapter 5. We focus solely on the unetched sample of GaAs on sapphire. OPNMR and NMR experiments were conducted in the homebuilt optical NMR probe (Chapter 3) which was inserted into a Janis CDNT-NMR optical cryostat. The cryostat was mounted to an 89-mm bore high homogeneity 3.0 T Oxford superconducting magnet. All experiments were conducted with the sequence depicted in Figure 3-8 with 4 μs 90° pulses, and 8 minutes of optical pumping time. All signals were measured were single scans, with approximately 112 mW cm\(^{-2}\) at the sample space.

**Strained-Induced Valence Band Splitting in the OPNMR Action Spectra of GaAs/Sapphire**

The OPNMR action spectra are plotted in Figure 6-1 for both the surface (black) and the interface (red) of the unetched (i.e. non-thinned) sample. Noticeably, for both the interface and the surface, there is an inversion where the OPNMR signal changes sign for irradiation with for \(\sigma^-\) light. There is also another inversion for \(\sigma^+\) light at the interface. A signal inversion for the OPNMR enhancement has never been reported in the literature for unstrained bulk GaAs at this temperature and field.\(^3\)\(^,\)\(^23\) We hypothesize that the origin of the observed inversions is from strain-induced splitting of the valence bands. The strain can split the bands, which creates a resonance offset that prevents simultaneous pumping of transitions to both spin up and spin down spin states in the conduction band.
Figure 6-1. The OPNMR action spectra of the GaAs/Sap composite at 3.00 T and 1.5 K. The red trace is the interface and the black trace is the surface. All OPNMR experiments were collected with 8 min of pumping time and approximately 35 mW at the sample.
The heavy hole and light hole bands in bulk GaAs are degenerate at \( k = 0 \). With the application of strain, the heavy hole and light hole are split by some energy \( E_{vh} \). The valence band splitting can be written as:

\[
E_{vh} = 2b\varepsilon \frac{C_{11} + 2C_{12}}{C_{11}}
\]  

(6-1)

where \( b \) is the deformation potential, \( C_{ij} \) are elements from the elastic tensor, and \( \varepsilon \) is the in-plane strain. To relate to \( \varepsilon_{zz} \), we use

\[
\varepsilon_{zz} = \frac{2C_{12}}{C_{11}} \varepsilon \, .
\]  

(6-2)

For GaAs, \( C_{11} = 118 \text{ GPa} \), \( C_{12} = 53.6 \text{ GPa} \), and the shear deformation potential \( b = -1.7 \text{ eV} \) as reported by Pollak and coworkers.\(^{82}\) From these numbers, the splitting was approximately 0.4 meV for the surface and 1.1 meV for the interface. According to the action spectra (Figure 6-1), 0.4 meV barely splits the light hole and heavy hole bands beyond their level broadenings, but 1.1 meV does split the band significantly, hence leading to the observed OPNMR signal inversion.

The relationship of strain to the inversion of the OPNMR signal is illustrated in Figure 6-2. The top portion is a simplified band diagram at \( k = 0 \) for GaAs. The bottom portion shows the changes in the levels due to biaxial tensile strain. In the diagram, for unstrained GaAs, the degeneracy of the light hole and heavy hole bands allows simultaneous pumping into the \( | \pm 1/2 \rangle \) conduction band spin states at a single photon energy. As noted earlier, this limits the electron spin polarization to \( \pm 0.25 \), which is 50% of its maximum value.
Figure 6-2. The associated energy levels of GaAs at \( k=0 \) for the unstrained (top) and strained case (bottom). The red arrows are the associated transition for a photon with \( \sigma^+ \) polarization, and the red numbers correspond to the probabilities of its respective transition according to the optical selection rules. Note that in the strained case, the strain causes an energetic barrier that prevents the transition from \( |-3/2\rangle \rightarrow |-1/2\rangle \) and only allows for spin-selective pumping of the \( |1/2\rangle \) state.

Although the application of a strong magnetic field produces a small valence band splitting, it is not enough to resolve the levels. Moreover, these effects are observable in the OPNMR action spectrum, but only as oscillations in the OPNMR signal.\(^{23}\) However, strain can produce a much larger valence band splitting, allowing for selective pumping of optical transitions to either \( |+1/2\rangle \) or \( |-1/2\rangle \). This implies that the conduction electron spin polarization will change sign with increasing photon energy. This directly impacts the OPNMR signal, as the relative sign of the photoelectron spin polarization affects the nuclear spin polarization. Recall from Equation 1-19, that \( I_z \) is related to the photoexcited conduction electron spin polarization, \( S_z \) by,\(^2\)
\[
\frac{dI_z}{dt} = \frac{1}{T_i^{\sigma_i}} \left[ I_z - I_{eq} - \frac{I(I+1)}{S(S+1)} (S_z - S_{eq}) \right]
\]  

(6-3)

where \( T_i^{\sigma_i} \) is the hyperfine cross-relaxation time constant, \( I_{eq} \) and \( S_{eq} \) are the equilibrium nuclear and electronic spin polarizations, and \( I \) and \( S \) are the nuclear and electronic spin numbers. From Chapter 2, the optical selection rules for unstrained GaAs limit the value of \( S_z \) to -0.25 for \( \sigma^+ \) polarization and +0.25 for \( \sigma^- \) polarization.\(^{29}\) At 1.5 K, the equilibrium spin polarization is approximately 0.14.\(^{29}\) At 1.5 K, the equilibrium spin polarization is approximately 0.14. Therefore, \( \sigma^+ \) photons cause \( \frac{dI_z}{dt} \) to be negative and yield negative (emissive) OPNMR signals. For \( \sigma^- \) photons, the converse applies, revealing positive (absorptive) signals. If the strain-induced valence band splitting is large enough, then the OPNMR signal should invert with changing photon energy while conserving the polarization of the photon. We observe this phenomena in the action spectra in Figure 6-1.

Notably, the effect described should be symmetric upon reversing the helicity of the photon polarization. From the data, it is seen not be symmetric. A possible explanation is band warping effects. Ideally band warping should not be significant for a biaxial strain.\(^{35, 36}\) Electronic band structure calculations are needed to help elucidate why the inversion is not exactly symmetric with respect to changing the polarization.

**Photon Energy Dependence of the Quadrupolar Splitting**

Exhibited in Figure 6-3 is a bitmap projection representation of the spectra of the Ga-71 near the surface and the interface acquired with \( \sigma^+ \) polarization at a series of photon energies for the unetched sample. In addition to the change in the OPNMR signal intensity, the apparent quadrupolar splitting also varies significantly. At the
surface, the quadrupolar splitting is seen to gradually decrease from 8.2 kHz to 4.2 kHz as the photon energy is increased from 1.50 to 1.52 eV. A qualitatively different trend is observed for the buried interface: at energies between 1.49 and 1.50 eV, the apparent quadrupolar splitting slightly increases, exhibiting broad satellite transitions, and then near 1.51 eV there is an abrupt narrowing of the lines to a well-defined quadrupolar splitting of sharply transitions to 11.8 kHz. These observations are associated with the change in penetration depth of sub-band gap photons together with gradients in the strain throughout the sample, which are different at the surface and at the interface.\textsuperscript{14, 79}

Figure 6-3. A bitmap projection of the action spectra for the surface (A) and interface (B) for $\sigma^+$ light. Blue indicates negative, red is positive, and the hue represents the magnitude.

The quadrupolar splitting observed in the OPNMR spectrum is a reflection of the local strain in the detected volume of the sample. At photon energies below the band gap of GaAs, photons penetrate farther into the sample.\textsuperscript{14} Under these consequences,
the OPNMR experiment probes a larger volume and hence a larger distribution of strains. The apparent quadrupolar splitting originates from the superposition of spectra from multiple layers leading to a heterogeneously broadened spectrum. Therefore, the spectra will contain a distribution of splittings with some apparent quadrupolar splitting, which will have a broader linewidth due to the distribution of strains. Satellite transitions of the $I = 3/2$ spin are affected by the quadrupolar interaction, while the central transition ($|\pm 1/2\rangle \leftrightarrow |\mp 1/2\rangle$) according to first order perturbation theory, is invariant, as both the $|\pm 1/2\rangle$ and $|\mp 1/2\rangle$ eigenstates are shifted in energy by the same amount equally (see Figure 1-2).

The data depicted in Figure 6-3 are consistent with the optical penetration depth interpretation, since the strain is larger at displacements far from the surface. As the photon energy increases, the probed volume is increasingly dominated by layers close to the surface, until it is predominantly only the surface, with lower strain, that is observed. The photon energy dependence of the apparent quadrupolar splitting for irradiation through the sapphire exhibits roughly the reverse trend: smaller splittings are further away from the buried interface and larger splittings occur at or near the interface. Furthermore, the linewidths of the satellite transitions drastically reduce once the photon energy is above the band gap, suggesting that the strain probed is uniform and localized near the interface. This is expected for the surface as well, but the overall magnitude of the quadrupolar splitting is too small for the satellite transitions to be resolved.
Inferring the Absorption Spectrum from the Quadrupolar Splitting

It can be seen in Figure 6-3B that all three Ga-71 transitions of the OPNMR spectrum are fully resolved for all photon energies in the experiment. The apparent quadrupolar splittings were fitted for each OPNMR spectrum using Massiot's DMFit\textsuperscript{83}. In this process, three Gaussian peaks were used to fit the satellite transitions and the central transition. The apparent quadrupolar splittings from each spectrum are plotted as a function of photon energy in Figure 6-4. The quadrupolar splitting reveals important information about the characteristic optical penetration depth, which is the inverse of the absorption coefficient. Furthermore, according to the mechanical bowing model, the strain gradient for a sample of fixed thickness and curvature is linear. Here, the sample thickness is fixed, in contrast to the results presented in Figure 5-3, where...
the GaAs layer thickness was varied. For a fixed sample thickness, the gradient in the strain across the sample is constant shown in Figure 6-5. With this knowledge of how the strain relaxes from the interface, the quadrupolar splitting can be used to infer the photon penetration depth in the sample for a given photon energy. Hence, an approximate optical absorption spectrum can be deduced from the quadrupolar splitting observed in the OPNMR spectra.

![Figure 6-5](image_url)

**Figure 6-5.** Left is the strain gradient throughout a composite with various curvatures. Right is the calibration model used to relate the quadrupolar splitting to the displacement from the interface.

Using the linear relationship between the quadrupolar splitting, $\Delta v_0$, and the displacement, $d$, from the interface, the following expression can be written:

$$\Delta v_0 = \frac{\Delta v_{0,I} - \Delta v_{0,S}}{t_0 - t} d + \Delta v_{0,0}$$  \hspace{1cm} (6-4)$$

where $\Delta v_{0,I}$ is the quadrupolar splitting at the interface, $\Delta v_{0,S}$ is the splitting at the surface, $\Delta v_{0,0}$ is the y-intercept, $t$ is the total thickness of the GaAs, and $t_0$ is the theoretically smallest volume probed by OPNMR at the interface. From discussions in
Chapter 4, we deduced that when accounting for diffusion effects along with the optical penetration depth, the lower limit of the thickness probed was 5.2 μm. Therefore, \( t_0 \) will be set to 5.2 μm for these calculations. The displacement approximates the optical penetration depth which is the inverse of the absorption coefficient. Therefore, Equation 6-4 can be rearranged to obtain the absorption coefficients in terms of the observed quadrupolar splittings and sample dimensions:

\[
\alpha = \left[ \frac{t-t_0}{\Delta v_{Q,s} - \Delta v_{Q,l}} \left( \Delta v_{Q} - \Delta v_{Q,0} \right) \right]^{-1}.
\]  \hspace{1cm} (6-5)

In Equation 6-5, using \( t_0 = 5.2 \) μm, we found \( \Delta v_{Q,0} = 11.89 \) kHz. Unfortunately, we cannot just fit the data and calculated the absorption coefficients as the spectra represent signals originating from multiple layers. Instead, we can use the relationship from Eq. 6-5 in combination with a weighted summation of simulated spectra to approximate the absorption coefficient. In this fitting procedure, we sum over 363 simulated spectra (one for each micron of the GaAs) to fit the data and extract an absorption coefficient. All 363 simulated spectra had a different quadrupolar splitting ranging from 11.89 kHz to 4.20 kHz, reflecting the location within the composite as described in Equation 6-4. The weighting factor for the summation was an exponentially decaying term, corresponding to the absorption coefficient.

Mathematically, the simulated spectra \( G(x, \Delta v_Q, a) \), were defined as

\[
G(x, \Delta v_Q, a) = 2a \exp \left[ -x^2 / \lambda^2 \right] + a \exp \left[ -(x - \Delta v_Q)^2 / \lambda^2 \right] + a \exp \left[ -(x + \Delta v_Q)^2 / \lambda^2 \right] \hspace{1cm} (6-6)
\]
where \( x \) was the frequency domain, \( \Delta \nu_q \) was the splitting for the spectrum, \( \lambda \) was the linewidth (set to central transition linewidth of 2.6 kHz), and \( a \) was the weighting factor. We minimized the residuals using the following summation, where \( \alpha \) was the free parameter:

\[
\sum_{j=1}^{363} G(x, \Delta \nu_{q,j}, e^{-j\alpha}).
\] (6-7)

Therefore, by adjusting the absorption coefficient (\( \alpha \)) of the weighted summation, we can fit the data and deduce the optical absorption spectrum. The inferred optical absorption spectrum is exhibited in Figure 6-5. The band gap from this absorption spectrum is 1.5089 eV, which agrees qualitatively well with calculations performed by Sun and Nishida for a tensile strain.\(^{36}\) Importantly, it should be noted that in regions of low optical absorption (blue region of Figure 6-4), the quadrupolar splitting is the a distribution of quadrupolar splittings over multiple layers. In this region, the absorption arises from impurities and therefore, the penetration depths below the band gap may have larger uncertainties.

Lastly, presented in Figure 6-7 are three spectra fitted spectra from the fitting at the experimentally observed band gap, above the band gap, and below the band gap. The fits of data at and above the band gap are in good agreement with the experimental spectra, and the apparent the quadrupolar splittings matches within 300 Hz (well within the \( \sim3\)kHz linewidth). Noticeably, the relative integrals of the lines should be 3:4:3 under thermal equilibrium conditions; however, the measured integrals are approximately 1:2:1. This could potentially arise from hindered spin diffusion.\(^{79,84}\) Goto recently reported OPNMR measurements of GaAs at the strained interface of
GaAs/InGaP, where a blockade of the nuclear spin diffusion was attributed to the strain gradient and prevented the 3:4:3 ratio.\textsuperscript{79}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{AbsorptionSpectrum_GaAs_Sapp.png}
\caption{Calculated absorption spectrum at the interface of the GaAs/Sapp composite using the weighted summation fitting presented in Equations 6-6 and 6-7.}
\end{figure}

Furthermore, the experimental linewidths appear to be broader than the values predicted from the simulation. However, the simulations at and above the band gap are able to quantitatively reproduce the lineshape and the observed quadrupolar splitting. As expected, due to the limitations of the experiment, the agreement between the below band gap simulation and experimental lineshape performs is not quite as good. The signal below band gap arises from impurity absorption and therefore a single exponential decay may not properly describe the attenuation of the light through the sample, especially depending on the different types of impurities and their relative oscillator strengths. From the fit, the breadth of the satellites is properly reproduced but
it appears that the amplitudes are not, especially near the maximum. Further work could investigate this effect and possibly be modelled in future work.

Figure 6-7. The simulated OPNMR lineshapes with photon energy below the band gap (blue), at the band gap (black), and above the band gap (red). The lineshapes should change as the absorption coefficient changes and probes more/less of the volume near the interface.

Conclusions

Epoxy-bonding GaAs to sapphire at high temperature and then cooling to cryogenic temperatures induces strain in the composite. Furthermore, the strain varies across the composite, as predicted by the elastic strain model. From the selectivity of the OPNMR experiment, we were able to measure local strain at the interface and surface. For the interface, the strain was large enough to split the valence band so that
it inverted the nuclear spin polarization with varying photon energy. However, the asymmetry of this inversion needs to be compared to electronic band structure calculation to fully understand the pertinent photo-physics.

Finally, we were able to deduce the optical absorption spectrum from the observed variation of the apparent quadrupolar splitting with the photon energy. Simulations to validate the absorption spectrum showed quantitative agreement with experimental data acquired with photon energies at and above the experimentally observed band gap of the bilayer. Furthermore, the simulations also showed qualitative agreement at photon energies below the band gap of the strained bilayer.
CHAPTER 7
CONCLUSIONS AND OUTLOOK

From this work, it is self-evident that OPNMR is a powerful tool for investigating not only thin films, but also the electronic band structure and microscopic local strain in a material. This chapter will summarize the conclusions of each chapter and suggest future experiments that could be performed.

In Chapter 3, a novel low temperature optically pumped NMR probe was fabricated which incorporates the use of optics within the cold space. The design features polarizing elements, along with gears to continuously change the polarization of light irradiating the sample. The probe’s base temperature was 1.5 K and the cryostat’s hold time was 10 hours. The base temperature of this probe affords larger OPNMR enhancements compared to most experimental setups found in the literature. Furthermore, the fiber based polarizing system eliminated any optical alignment procedures, providing for easier use. The cold polarization optics has potential applications outside of OPNMR as well, including uses for interrogating the NV centers in diamond.

The LIQR mechanism was heavily investigated in GaMnAs in Chapter 4. When irradiated with light, the signal in the 3.8% Mn sample increased but this enhancement was nearly invariant with polarization and photon energy. From our investigation, we attempted to determine if LIQR was favored or if there was a total lack of OPNMR. We investigated, the diffusion of the LIQR signal and saw it was slower in comparison to bulk GaAs. Furthermore, we also investigated whether the electrical acceptors in GaMnAs accelerated nuclear spin relaxation in the material and investigated possible LIQR signals in p-type GaAs. No LIQR signal was ever found in p-type, indicating that
the LIQR observed in the 3.8% Mn sample did not originate from the electrical acceptors. Therefore, our results suggest that the LIQR mechanism was not favored, but rather OPNMR does not occur in the 3.8% Mn sample at all. Further experiments should investigate similar systems including CdTe and CdMnTe as neither Cd or Te are quadrupolar nuclei.

Chapter 5 focused on measuring the local strain in GaAs/Si composites using OPNMR. Using the relationship between the EFG and a biaxial strain, we showed that the strain is directly proportional to the quadrupolar splitting observed in the NMR or OPNMR spectrum. With this relationship known, we then investigated how the strain relaxed in the composite. We tested two possible models: a dislocation propagation model and a mechanical bowing model. We prepared a series of samples with varying GaAs thickness to investigate these models.

The initial data suggested the mechanical bowing model was the dominant relaxation mechanism in the composite. Therefore, we investigated the quadrupolar splitting dependence on the Si thickness. From the results, we observed an increase in the quadrupolar splitting with increasing the Si thickness, which can only be explained with the mechanical bowing model. Therefore, from the study in Chapter 5 we conclude that the data suggests the dominant relaxation mechanism was a mechanical bowing model.

However, in this study, one important feature that was not conserved was the aspect ratio between the two layers. The etchant used in our work was an isotropic etchant: removed material in all three dimensions equally. Fortunately, the epoxy wicked up along the edges of the GaAs when curing and acted as a protective coating.
once cured. This wicking caused a preferred etching direction from the surface of the GaAs. Unfortunately, very thin samples displayed obvious etching from the sides. We hypothesized that voids in the protective wick along the side allowed for edge-on etching. Ultimately, the etching could cause the aspect ratio between the two layers not to be conserved. Therefore, a future experiment could be to prepare a series of GaAs/Si samples with same thickness but varied aspect ratios and investigate the resulting strain.

And finally, in Chapter 6, we extended the work from Chapter 5 but by changing the substrate from the optically opaque Si, to the transparent Sapphire. Epoxying GaAs to Sapphire at high temperature and then cooling to cryogenic temperatures induces strain in the composite, similar to the GaAs/Si samples. Furthermore, the strain varies throughout the material. From the selectivity of the OPNMR experiment, we were able to measure local strain at the interface and surface. From the observed findings, the nuclear quadrupolar splitting showed that the splitting at the interface was almost tripled that of the surface for the unetched sample. For the interface, the strain was large enough to split the valence band such that it inverted the nuclear spin polarization with varying the photon energy.

Furthermore, using the variation in the quadrupolar splitting with photon energy and knowledge of how the strain relaxes from the interface, we approximated a qualitative absorption spectrum. Simulations to validate the absorption spectrum showed qualitative agreement with measurements at and above the experimentally observed band gap for the strained sample. Future work will focus on addressing whether the strain magnitude affects the nuclear spin diffusion.
APPENDIX A
INSTRUMENTATION AND AUTOMATION OF THE ACTION SPECTRUM

This appendix describes in detail how to use the automation system for collection of the action spectrum – i.e. the optically pumped NMR signal as a function of the photon energy. Considerable attention is given to the individual components that collectively form the automation system. Furthermore, proper operation and user tips are given.

The Action Spectrum Automation
The Coherent 899-01 Ring Laser was automated using an Arduino microcontroller (Arduino Uno board R3, purchased from Adafruit) and two stepper motors (NEMA-17, 200 steps/revolution, purchased from Adafruit). The motors were driven using the Adafruit Motorshield (Adafruit, Version 2.0). The motorshield is a stackable add-on that allows operation of two different stepper motors simultaneously. The overall scheme of the automation is to tune the laser to a new wavelength while maintaining constant optical power, and finally, to acquire the NMR spectrum. NMR spectra were acquired using a Tecmag Scout™ NMR spectrometer. (Serial no. 38086, Tecmag Inc, Houston, TX). This section describes the second (and current) version of this automation system. In the now obsolete first version, the Scout spectrometer would wait for a TTL input before acquiring the spectrum. Unfortunately, a bug in the Tecmag Scout restricted the maximum delay that could be used (c.a. 47 s), so a work-around had to be found. In the second version, the automation has been rewritten to have Labview open the TNMR software to execute acquisition of the FID.

The automation script utilizes a stepper motor to rotate the birefringent filter to change the laser wavelength. The output power is monitored using a small reflection off
a borosilicate plate (Chemglass) onto a thermopile photodetector (Thorlabs Model D3MM, Serial no. GP55), where the analog output is digitized by a National Instruments DAQ (USB-6008, Serial no. 181F284) and read by Labview. A neutral density filter wheel that is coupled to the shaft of the second stepper motor is placed at the output of the laser, and the wheel is rotated to vary the attenuation to match the specified output power. Once the laser power reading falls within a user-specified acceptable range, Labview will initiate the OPNMR pulse sequence and acquisition of the NMR spectrum. There are three levels of programming code used in this automation: 1) code for the Arduino 2) Labview code 3) and Tecmag OLE (object linking and embedding).

**Arduino Code**

The Arduino needs to control two stepper motors independently of each other. Controlling the two motors independently required the “Adafruit MotorShield (V2)” library and the “TextFinder” library. The motorshield drives the physical stepper motors, while the textfinder is used to read an inputted string of two numbers from Labview (communicated via USB connection to the computer). The two numbers correspond to the number of steps for the two different motors. For example, (100, -200) would correspond to 100 clockwise steps forward for the M1 motor, and 200 steps counterclockwise steps for the M2 motor. The Arduino runs this code in a continuous loop as shown in Figure A-1, and therefore can interrupt itself in the middle of a slew if it receives a new input of numbers. This is desired in case the user wants to stop the motors for any reason. Lastly, the stepping speed has been set to 100 rpm. This is the fastest speed the stepper motor can provide and still effectively drive the shaft coupled to the birefringent filter.
Figure A-1. Sample of Arduino code used to read the serial communication from Labview

```c
motor2->setSpeed(100); // 100 rpm
//Define directions of forward and backwards in terms of steps
void loop()
{
    int fieldIndex = 0;  // the current field being received

    while(fieldIndex < NUMBER_OF_FIELDS|
        values[fieldIndex++] = finder.getValue());

    if(values[0] < 0 )
    {
        dir1 = BACKWARD;
        steps1 = -1 * values[0];
    }
    else
    {
        dir1 = FORWARD;
        steps1 = values[0];
    }

    if(values[1] < 0 )
    {
        dir2 = BACKWARD;
        steps2 = -1 * values[1];
    }
    else
    {
        dir2 = FORWARD;
        steps2 = values[1];
    }

    // Serial.println( steps1);
    // Serial.println( steps2);
    motor1->step(steps1, dir1, SINGLE);
    motor2->step(steps2, dir2, SINGLE);
```

Labview Automation Front Panel

The front panel of the Labview program is exhibited in Figure A-2. The user needs to first input the range of the laser wavelength of interest in the “Maximum Wavelength (nm)” and “Minimum Wavelength (nm)” controls. The step size indicates the minimum step between experiments. The automation is designed to work with a minimum step size of 0.25 nm. The “Power Meter” and “Arduino” drop-down controls
allow the user to select the proper device/communication port for the DAQ/Arduino. To find this information, go to the Control Panel and select “View devices and printers”. The “% Tolerance” defines the acceptable threshold before the NMR experiment is started. In the figure, the tolerance is set to 5%, meaning that the optical power must be within +/- 5% of the target power. Lastly, two files must be selected before the experiment is started. The “Output of Power Record” is used to identify which experiments did not converge within the “% Tolerance”. For example, if the power was too low that the automation was never able to reach the “Target Power”, then after 25 iterations of attempting to converge, the automation will stop adjusting the optical power and continue to the next portion of the automation. This data entry will be flagged though in the output report as a failed experiment.

The “NMR Template File” is a 1-D NMR file (a. tnt file type, generated in the TNMR software). This experiment file is repeatedly acquired (with different photon energies) to create the action spectrum. Once the optical power converges to the target power, Labview communicates to the TNMR software (using the OLE’s) to open and “ZG” the file located in the “NMR Template File”. TNMR will then acquire the FID using the parameters and pulse sequence in the template file. Once the acquisition is finished, the NMR data will be appended to a file with the same filename as the template file but with “-2D.tnt” added to the end. Each iteration of the automation is appended to this file to generate a 2D NMR spectrum (i.e. an array of 1-D spectra). The filename of the 2-D spectrum will appear in the “Output 2D File” field.
Labview Automation Operation

Before starting the Labview automation, the laser must be tuned to the lowest wavelength of interest to begin the OPNMR action spectrum. The automation is designed to run from low wavelength to high wavelength. This is to ensure that the signal-to-noise ratios of the OPNMR spectra will be sufficiently high over the entire photon energy range of the study. As the wavelength increases, the OPNMR signals are generally more intense due to the greater volume of penetration of the light into the sample. Furthermore, it is recommended to measure the optical power using a second power meter (not the meter incorporated in the automation). The “zero” on the automation thermopile drifts with long periods of time and may need to be re-zeroed. Using the second power meter ensures the device is properly zeroed.
To start the automation, click hit he “Run” button (arrow in upper right). The user is prompted to verify that the optical power is acceptable. If so, click OK to run the Labview program. The status LED’s on the Front panel indicate whether the automation is adjusting the power or acquiring the NMR spectrum. Furthermore, the optical power of the laser with each iteration of the automation is presented on the graph in the front panel.

**Labview Code**

A summary of the Labview automation code is presented here. The first part of the code is the initialization of the parameters entered on the front panel: wavelengths of interest, step size, NMR template file, etc. (see Figure A-2). The next portion of the code is the looped sequence table. In the sequence, Labview tunes to a new wavelength (except on the first iteration) and then reads the optical power. If the optical power is too high or low, then Labview will command the Arduino to move the neutral density filter to change the optical power. There are two adjustments, “Large Adjust” or “Small Adjust”, which depend on the deviation away from the target power. Once within the tolerance, Labview will then open the TNMR software which will then acquire and save the data to the 2D file. If the power fails to converge to the target power, the feedback loop will timeout, and proceed to acquire the NMR spectrum. This spectrum will be flagged in the Output Record as a failed experiment. After acquisition of the NMR spectrum, the sequence will loop back to the beginning of the sequence table and repeat this for the user specified number of wavelength steps ((Max Wavelength-Min Wavelength)/Step Size).
Tecmag OLE’s and Labview

The TNMR software supports the use of object linking and embedding (OLE) in the Microsoft Windows 7 & 10 operating systems. This allows Labview to open documents and run macros in TNMR. In Labview, the ActiveX palette is used to access the TNMR OLE’s. The block diagram of the acquisition is shown in Figure A-3. Multiple OLE’s are utilized: first the spectrometer is zeroed, and the acquisition is started (“ZeroAndGo”). Then Labview sits in a For Loop until the “CheckAcquisition” finally reads true (i.e. it is no longer acquiring a spectrum). The acquired data are appended to the 2D file using the “AppendToFile” OLE and are finally saved. An important note when running the Labview automation is that it does not open the template file after each iteration. The filename is called only once at the beginning of the automation. Furthermore, the “ZeroAndGo” OLE begins acquisition of the “active” window in the TNMR software. Therefore, it is not recommended to browse the dataset in the TNMR software while the automation is running, as it may attempt to acquire the 2-D NMR file. This would result in acquisition of multiple data points at one photon energy which is not desired. For example, if the automation had collected 25 spectra at various wavelengths and the 2-D file was active when “ZeroAndGo” was evaluated, it would acquire that 2-D experiment, which would overwrite the previous 25 spectra with spectra recorded all at the same wavelength. It is recommended to save the data to a new filename and browse using MNova or another program.
Figure A-3. The block diagram used for the automated collection of NMR spectra using Labview.
This section describes the automation of the McPherson monochromator utilized for optical spectroscopy in this dissertation. The original software for the McPherson 207 Monochromator was written for Windows 95 and is obsolete for modern machines. Working with the employees at McPherson, we were able to automate the monochromator again. The current Labview VI is mostly their design, except for the detection scheme. Currently, the detection scheme utilizes a DAQ to read the input of photomultiplier tube or the readout of a Lock-In amplifier. Therefore, the following sections will focus on the use and acquisition of optical spectra.

**Hardware Setup**

A McPherson 207 scanning monochromator (McPherson Inc., Serial # 207-69, Chelmsford, MA) was automated using a stepper motor and a driver. The stepper motor moves the grating, which is controlled with the Labview driver over a RS232 DB-9 pin connector. A USB-to- RS232 serial converter (Prolific) connects the driver to the computer. The light passed to the exit slit is collected with a side-on McPherson Inc. Model 654 photomultiplier tube (rise time is 2.2 ns, and maximum bias voltage is -1250 VDC). In the case of absorption spectroscopy, the output of the photomultiplier tube (PMT) is fed to a Lock-In amplifier (Stanford Research, Model SR850). An optical chopper is used to modulate the light, and the output of the Lock-In is read by the DAQ. Enhancements in signal-to-noise using the Lock-In are on the order of 2000. For photoluminescence experiments, the Lock-In can be avoided and the PMT output can be directly connected to the DAQ (default input channel is A7). Lastly, the DAQ sampling rate is 5 kHz.
Monochromator Operation and Use

The front panel of the Labview code is depicted in Figure B-1. The A-3 com port is the port of the Prolific USB-RS232 converter. Use the Control Panel to properly identify which com port it is. The “Configuration path” is the path directory to the configuration file. The configuration file is a text file that contains important information about the system, including turns per nanometer, number of grooves on the grating and other information. The configuration file will be described in greater detail later. Before running the Labview program, the configuration file path must be properly set or else the program will give an error when attempting to execute. Once the path is set, press run (Arrow upper left).

On the front panel, there are two sub-panels: the Motor Controller and the Scan controller. The Motor Controller has three important controls: “Counter Reading”, “Current Position”, and “Target Position”. The Labview program has no internal feedback to ensure that the monochromator is on the correct wavelength and these three help maintain correct performance. On the monochromator frame is a small black turn counter that correlates to the passing wavelength (this was last calibrated on August 2017 using the lines of a low-pressure Hg lamp). The “Counter Reading” in the Labview program can be used to adjust the “Current Position” so it matches the physical counter reading (black turn counter on the monochromator). The “Counter Reading” acts as an adjustment feature for the “Current Position”. After adjusting the “Counter Reading”, the “Current Position” should update to the correct value. Ideally, the “Counter Reading”, “Current Position”, and physical counter should all match under normal operation. If the “Counter Reading” needs continual adjustment, either the configuration file is wrong, or the monochromator needs to be calibrated/serviced.
Lastly, the “Target position” is a useful tool to check if the monochromator will properly move to a desired wavelength. Simply type the desired wavelength and press “Set Position”. The monochromator should step to the target wavelength. The “Stop” button will stop the movement in the middle of the slew.

Figure B-1. Front panel of the Labview program for the monochromator

The Scan Controller is useful for optical spectroscopy. Type in the beginning and ending wavelengths of the desired wavelength range and choose the increment size. The smallest increment size will be limited by the grating and slit width. The bandpass is limited by the product of the slit width and reciprocal linear dispersion of the grating. For this grating (1200 grooves/mm), the reciprocal dispersion is 1.24 nm/mm. A 5 μm slit width yields 0.0062 nm resolution.

The detection method utilizes the output of a PMT to a DAQ. Choose the DAQ in the dropdown at the bottom left. The signal is integrated over the desired Exposure
time in units of seconds. The signal of the PMT is negative due to the negative bias potential of the PMT. Therefore, to give aesthetically pleasing results, the data is multiplied by -1 after acquisition. Depending on the spectroscopy, it may be useful to use a Lock-In amplifier. Therefore, a check-box labelled “Lock-In” is provided to remove the -1-multiplication factor. An important note for using a Lock-In is the time constant. The program is not interfaced with the Lock-In and operates independently of it. If the user picks a time constant that is very slow compared to the Exposure time, then the data will not be reproducible. Always make sure the exposure time is at least 5 times the time constant used on the Lock-In.

Finally, the Home button is a default button that forces the monochromator to its home wavelength (200 nm). This a designer function to ensure ideal behavior. To quit the program, press the Exit button. The exit button not only quits the program but edits and saves the configuration file so that, upon starting the program again, Labview will already know the “Current Position” of the monochromator.
Figure B-2. The front panel of the Graph portion of the Labview program for the monochromator

To properly visualize the data, a second tab is seen on the front panel called Graph, exhibited in Figure B-2. This allows the user to graphically visualize the data acquired in real-time. The data are exported via this page by right-clicking on the graph and pressing Export To. If the detector is saturated or if the experiment needs to be stopped for any other reason, the “Stop Scan” button can be hit. This button is found above the graph.

Configuration File

The configuration file is arguably the most important piece for the automation, because incorrect information within the file will cause poor performance of the instrument. The configuration file contains the information that determines how many steps are needed for the stepper motor to properly move to a new wavelength. This depends on the gearing, the steps per revolution, and ultimately the grating. A working
configuration file is always saved on the desktop of the computer as a backup configuration, while the normal configuration file is the folder containing the program. An important realization from the configuration file is it gives the minimal mechanical resolution of the hardware (not accounting for the slit width size). According to the configuration file exhibited in Figure B-3, there are 36000 steps per revolution and 5 nm per revolution. Therefore, the monochromator has mechanical resolution down to 0.00014 nm, given an infinitely thin slit width. However, typical laboratory experiments use a 5 μm slit width which causes an increase in the bandpass, limiting the resolution to 0.0063 nm.

![Configuration File Example](image)

Figure B-3. An example of a working configuration file
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

John T. Tokarski III was born and raised in Pittsburgh, PA where he attended public school throughout his youth. In 2009, John enrolled at Washington & Jefferson College, where he studied chemistry while playing collegiate football. At Washington & Jefferson, John joined the research lab of Robbie Iuliucci in the summer of his sophomore year. As a member, John conducted research in the field of solid state NMR, where he attempted to rebuild the chemical shift anisotropy tensor to form crystallographic information of the drug cimetidine. John would eventually go on to study abroad in the Netherlands, where he conducted research under the tutelage of Arno Kentgens, still within the field of solid state NMR. Upon returning to the United States, John graduated with his bachelor's degree in chemistry in May of 2013 and enrolled into the University of Florida as a graduate student that Fall. John was mentored by Russ Bowers from 2013 until 2019, upon earning his PhD in chemistry.