Current-Induced Dynamic Nuclear Polarization: Spintronics without Magnetism

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To my parents
Abstract

The present work deals with the study of Dynamic Nuclear Polarization (DNP), especially current-induced DNP, in III-V semiconductors such as InP and GaAs. Localized electron centres in these semiconductors have extended wavefunctions and exhibit strong hyperfine coupling with the nuclei in their vicinity. These interactions not only play a critical role in electron and nuclear spin relaxation mechanisms, but also enable nuclear polarization enhancement via DNP. The doping concentration and temperature range favourable for DNP effects was determined by studying these semiconductors with varying doping concentration in a wide temperature range. Under suitable conditions, DNP enhancement by more than two orders of magnitude was observed by microwave saturation of electron spin transitions in InP. Additionally, we report the first experimental observation of electric-current induced DNP in InP. This is consistent with model predictions in zinc-blende semiconductors with strong spin-orbit effects. This provides a promising possibility to generate spin polarization by means of electric current and hence is an important step towards an "all electric spintronic device".

Analogous to the spin Hall effect, the “spin Gunn effect” was proposed theoretically in III-V semiconductors recently. A small spin polarization is expected to grow and lead to spin polarized domains within the Gunn regime. If demonstrated experimentally, the spin Gunn effect can open a wide range of possibilities in the field of spintronics. We investigated the possible existence of spin Gunn effect in InP and GaAs by means of pulsed NMR measurements. From our measurements we conclude that the electron spin polarization and the resulting DNP effects appear to be much smaller than the theoretical predictions.
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Chapter 1

Introduction

Efficient manipulation of spin polarized currents and its eventual application in the magnetic storage industry is the ultimate goal for the field of spintronics. Conventional spintronic devices utilize ferromagnetism for generation and manipulation of spin polarization. After immense pioneering work spanning over three decades, devices which incorporate ferromagnetic elements for injecting, detecting and manipulating spins have been proposed and successfully demonstrated\(^1\).

Recent discoveries\(^{27,139}\) in spintronics, however, have triggered a quest for ‘spintronics without magnetism’. The motivation for this branch of spintronics is to realize an all-electric spintronic device. Spin-Orbit (SO) effects in semiconductors provide a promising possibility to generate and manipulate carrier spins in semiconductors without involving any ferromagnetism. These effects acting on a normal current flowing through a semiconductor give rise to spin polarization by means of two complementary effects: the Spin Hall Effect (SHE) and Current-Induced Spin Polarization (CISP). The spin polarized current can be further modulated by regulating factors such as electric field, strain and interfaces which modify the SO interaction.
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While the spin Hall effect results in spin accumulation at the edges of a semiconductor, CISP generates uniform bulk spin polarization within a semiconductor. Both these effects were predicted\textsuperscript{2,3} decades before being confirmed experimentally in a variety of semiconductors\textsuperscript{4,28,139}. While the experimental and theoretical studies have improved the present state of understanding of these phenomena, sufficient understanding needed to design materials with favourable parameters still evades us. Several experimental observations remain unanswered such as, in spite of a much weaker spin-orbit coupling parameter in ZnSe, current induced spin polarization can be observed in this material at room temperature in contrast to n-type GaAs. Thus, although complete understanding and successful technological application of these phenomena still remains a challenge, it offers an array of interesting scientific opportunities.

Apart from generation and manipulation of spin polarization, another essential requirement for spintronics devices is a long spin coherence time. Quantum coherence of spins in semiconductors is limited by coupling to their environment. The spin decoherence time of electrons in III-V semiconductors has been shown to be severely affected by the interaction with nuclear spins\textsuperscript{5}. The hyperfine interaction with nuclear spins has two independent effects on electron spins. Firstly, each nuclear spin exerts an effective magnetic field on the electron spin. This field, known as the Overhauser field can be as large as 5T in GaAs\textsuperscript{41} for complete nuclear polarization. Random fluctuations in this nuclear field result in spin dephasing time\textsuperscript{5} of the order of 10ns. Secondly, electron nuclear flip-flop processes result in electron spin relaxation via the nuclear spins. In the case where the electron spin polarization is continuously saturated (by microwave saturation for example), an enhancement of nuclear spin polarization is achieved. This transfer of spin polarization from the electron spin system to the nuclear spin system under suitable conditions is known as Dynamic Nuclear Polarization (DNP).

DNP has received increased attention by the EPR, NMR and microwave engineering community in the recent years. The growing importance of DNP can be judged from the vast variety of commercial hardware available in the market for \textit{in vitro} applications of DNP in spectroscopy and imaging as well as \textit{in vivo} applications in the medical MRI field. Several DNP strategies have been proposed till date and used successfully in conjunction with appropriate hardware to enhance sensitivity in a wide range of NMR, and MRI experiments. In semiconductor spintronics, however, study of DNP is relevant not for signal enhancement but for a different objective altogether.

Both electron and nuclear spins in semiconductors are favourable candidates for memory storage in spintronics and quantum computing
devices. While electrons allow fast manipulation, they have rather short coherence times. Nuclear spins on the other hand have much longer coherence times but are slow to manipulate and suffer from weak thermal polarization. The idea of using electron spins for processing and read out and using nuclear spins as 'memory reservoir' has been realized recently to enhance the memory lifetime. The transfer of spin polarization between electron and nuclear system is possible by means of dynamic nuclear polarization mediated by hyperfine coupling.

An essential requirement for the generation of DNP is to drive the electron spin system out of thermal equilibrium. While, microwave-induced ESR saturation is the preferred and the most frequently used method, III-V semiconductors with zinc-blende crystal structure offer another unique possibility of electron spin polarization in the form of CISP. The combined effect of CISP and DNP (current-induced dynamic nuclear polarization) results in an enhancement of nuclear polarization by electrons accelerated in a dc electric field. A thorough understanding of current induced dynamic nuclear polarization in III-V semiconductors is crucial for two reasons. Firstly, it will provide an electrical means of preparing spin-polarized carriers without magnetic materials and hence is an important step towards successful realization of all electrical non magnetic spintronic devices. Secondly, it is essential for understanding the detrimental effects of nuclear spins on coherence of electron spins in these semiconductors.

Analogous to the spin Hall effect, the “spin Gunn effect” has been proposed recently by Qi et al. in III-V semiconductors. The difference in electron mobility in the two valleys of these semiconductors drives the standard Gunn Effect. The electron mobility is however spin dependent in many semiconductors. Thus, a small spin polarization (created either by a random thermal fluctuation or spin-orbit effects) is expected to grow and lead to spin polarized domains. This is termed as the "spin Gunn effect" A theoretical calculation and prediction of this effect resulting in the generation of spin polarized current pulses in GaAs and InP was published recently. Within the spin Gunn regime, spin polarized domains extending in space to a few μm have been predicted InP and GaAs. Within such a spin Gunn domain, electron spin polarization of up to unity may be achieved. Since, the electron system is driven out of equilibrium; it has a tendency to relax to the equilibrium. In presence of strong electron-nuclear hyperfine coupling, the transitions of electron spin system towards thermal equilibrium are expected to dynamically polarize nuclear spins. The spin Gunn domains can thus be, in principle, detectable by measuring their effect on nuclear polarization. If demonstrated experimentally, the spin Gunn effect will open a wide range of possibilities such as generating a reservoir of spin-polarized
carriers within the semiconductor for spin-based logic, modulating the optical properties of semiconductor devices at high speed and exploring resonant transport through quantum dots.

Keeping these objectives in mind, we have carried out detailed experiments on two of the most commonly used III-V semiconductors, GaAs and InP to understand the mechanism of DNP processes in these materials in general and current-induced DNP in particular. Both these semiconductors have extended donor wavefunctions and exhibit strong hyperfine interaction with the nuclei in the vicinity of donors. Moreover, both InP and GaAs have zinc-blende structure and thus allow current-induced electron spin polarization. Theoretical concepts used for describing III-V semiconductors and understanding of current induced DNP in these semiconductors such as the effective mass theory, Dresselhaus and Rashba spin splittings and Feher effect are reviewed in Chapter 2. Chapter 3 outlines the magnetic resonance techniques such as Nuclear Magnetic Resonance, Electron Spin Resonance, Overhauser shift spectroscopy as well as the concepts essential to the understanding of dynamic nuclear polarization in semiconductors such as hyperfine interaction, spin diffusion and Overhauser effect. Temperature dependent measurements of resistivity and nuclear spin lattice relaxation rates in GaAs and InP are described in Chapter 4. These measurements elucidate the extent of localization of electrons and the dominant mechanism of nuclear relaxation for various nuclei in these semiconductors. Chapter 5 and 6 describe the Overhauser shift spectroscopy measurements on InP and Si:P respectively. In order to understand the interactions which are responsible for creation of dynamic nuclear polarization and Overhauser shifts in semiconductors, a quantitative model was developed using MATLAB. This is described in Chapter 7. Chapter 8 deals with the study of current induced dynamic nuclear polarization scheme in GaAs and InP. NMR measurements on InP bulk, GaAs bulk and GaAs Gunn samples were performed in order to investigate the spin Gunn effect and possible dynamic nuclear polarization generated by these domains. These measurements are discussed in Chapter 9. Finally in Chapter 10, the outcome of investigations described in this dissertation is summarized.
Chapter 2

III-V Semiconductors

In this chapter, the theory of III-V semiconductors is reviewed with an emphasis on concepts essential for understanding of this dissertation. Section 2.1 deals with the description of Effective mass theory, the most commonly used theory for the study of donor states in semiconductors. The preferred crystal structure for III-V semiconductors (zinc-blende) is described briefly in section 2.2. The inversion asymmetry of zinc-blende lattice lifts degeneracy of conduction band corresponding to spin $\uparrow$ and $\downarrow$. This lifting of degeneracy is the topic of discussion in section 2.3. The two types of spin splitting, (Dresselhaus spin splitting and Bychkov and Rashba spin splitting) are described in this section. Spin splitting of the conduction band provides a possibility of spin polarization by means of electric current in such systems. This is commonly referred to as Current Induced Spin Polarization (CISP). CISP in zinc-blende systems is briefly described in section 2.4. A nuclear polarization scheme based on the difference between the electron spin temperature and the temperature corresponding to the mean kinetic energy of the electrons accelerated in a dc electric field is introduced in section 2.5. This polarization scheme, known as the "Feher effect" lays the foundation of current-induced dynamic nuclear polarization in III-V semiconductors. Early experiments in the direction of creating current-induced dynamic nuclear polarization in III-V semiconductors from literature are listed in section 2.6.
2.1 Effective Mass Theory

The effective mass theory enunciated by Kohn and Luttinger\(^9\) is very useful in the study of impurity states in semiconductors. This theory in its simplest form assumes a hydrogen-like donor atom immersed in a dielectric background. The energy eigenvalues of such a system can be obtained using a potential \( V(r) \propto e/(\varepsilon(r) \cdot r) \) where \( \varepsilon(r) \) is the static dielectric screening function and \( r \) is the distance between the donor ion and electron. Since the static dielectric constant \( \varepsilon(r) \) and the effective mass \( m_{\text{eff}} \) at the bottom of the conduction band are around 10 and 0.1\(m_0\) respectively for a typical semiconductor, the impurity orbits are quite large (typically about 10nm). Hence the screening function may be replaced by a static dielectric constant in the potential energy term of the Hamiltonian.

The validity of effective mass theory requires:
- The effective Bohr radius must be greater than the lattice constant.
- The wave vector \((k)\) should lie close to the band minima so that the effective mass is well defined.
- The energy of the donors \((E_d)\) should lie close to the conduction band as compared to the band gap.

A quantum mechanical description of a substitution defect in a semiconductor is described below. The surplus electron in the host lattice follows Schrödinger equation

\[
\hat{H}\psi = E\psi 
\]  

with the Hamiltonian operator

\[
\hat{H} = \hat{H}_0 - \frac{e^2}{4\pi\varepsilon_d\varepsilon_0 r} 
\]

Here \( H_0 \) is the unperturbed Hamiltonian operator in the ideal lattice. In addition to that, we have a coulomb interaction with the defect which is weakened through the shielding of the lattice. \( r \) is the distance of the donor electron from the donor nucleus and \( \varepsilon = \varepsilon_d\varepsilon_0 \) is the dielectric constant of the medium. The solutions of the unperturbed Hamiltonian are the Bloch functions which form a complete Orthonormal System. Therefore, the solution of equation 2.1 may be written as a linear combination as follows:

\[
\psi = \sum_{n,k} c_n(k)\psi_n(k,r) \geq \sum_k c_c(k)\psi_c(k,r) 
\]

In good approximation only the eigenfunctions of the nearest conduction band are used to describe the donor states. Thus, summation over all the bands \((n)\) is not required. Thus, the Bloch functions of conduction band electrons appropriate for the description of the donor are:

\[
\psi_c(k,r) = u_c(k,r)\exp(ik \cdot r) 
\]
Since the wavefunctions are extended over many lattice constants in position space, the values of \( k \) vectors are restricted to near the centre of the Brillouin zone. In such a case \( u_c(k) \) is only weakly dependent on \( k \) and can be considered to be a constant for \( k \approx 0 \) and therefore can be written outside the summation.

\[
\psi(k,r) = \left\{ \sum_k c_c(k) \exp(ik \cdot r) \right\} u_c(k_o, r) = F(r)\psi_i(k_o, r)
\]  (2.5)

In equation 2.5, \( \psi_i(k_o, r) \) is the Bloch equation with the \( i^{th} \) minimum of \( E(k) \) and

\[
F(r) = \sum_k c_c(k) \exp(ik \cdot r)
\]  (2.6)

is a function representing the envelope of the wave packet. This function satisfies the Schrödinger equation of a quasi H atom

\[
\left\{ -\frac{\hbar^2}{2m_{\text{eff}}} \nabla^2 - \frac{e^2}{4\pi\varepsilon_o r^2} \right\} F(r) = (E - E_c)F(r)
\]  (2.7)

Here \( E_c \) is the energy of the conduction band and \( m_{\text{eff}} \) is the effective mass of the electron near conduction band.

This Schrödinger wavefunction describes the electronic state of a hydrogen atom with mass \( m_{\text{eff}} \) in a medium of dielectric constant \( \varepsilon \). The solution of eqn. 2.7 is therefore of the same form as that of hydrogen atom and for 1s state may be written as:

\[
F(r) = \frac{1}{\sqrt{\pi a_{\text{eff}}^3}} \exp\left(-\frac{r}{a_{\text{eff}}}\right)
\]  (2.8)

with

\[
a_{\text{eff}} = \frac{4\pi\varepsilon_o \varepsilon_{\text{st}} \hbar^2}{m_{\text{eff}} \varepsilon_o} = \frac{\varepsilon_{\text{st}} m_0}{m_{\text{eff}}} a_0
\]  (2.9)

and the Bohr radius \( a_0 = 5.29 \text{nm} \). The envelope wavefunction (dashed curve) and the total wavefunction (solid curve) is shown in Fig. 2.1. The total wavefunction shows the modulation with the rapidly oscillating Bloch function with a period length of the lattice constant 'a'.

The resulting eigenstates of the envelope function are bound states below the lowest free states in the conduction band \( E_c \) and are given by a quasi-hydrogen energy spectrum:

\[
E_d^n = E_c - \frac{m_{\text{eff}} e^4}{32\pi (\varepsilon_{\text{st}} \varepsilon_o)^2 \hbar^2} \left( \frac{1}{n^2} \right) = E_c - \frac{13.6eV m_{\text{eff}}}{\varepsilon_{\text{st}}^2} \frac{1}{m_0 n^2}
\]  (2.10)
Fig. 2.1: The envelope wavefunction $F(r)$ (dashed curve) and the wave function $\psi_n(r)$ (solid curve) of a Bloch wave packet for an electron localized near a hydrogen-like impurity. Here 'a' denotes the lattice constant. Figure taken from reference [10]

It is to be noted that EMT is a simplification of actual picture existing in a semiconductor. In reality, a number of refinements are needed in the ground state calculation using the hydrogenic effective mass theory to explain the experimental observations. For example, in elemental semiconductors, the mixing of hydrogen-like donor states with different subbands results in the splitting of the ground state. This splitting varies for different donors and is the largest contribution to the observed deviation of the ground state from the effective mass hydrogen like model in semiconductors such as silicon and germanium. Other corrections to the simplified model deal with the short-range actual potential of the impurity. Such central cell corrections include various attempts to:

- use modified dielectric screening for estimating the short-range potential;
- consider the strain field from the misfit of the impurity into a substitutional site; and
- introduce local pseudopotentials.

The envelope function defined above refers to the average nature of the wave function of the unpaired electron without consideration of the nodal structure inside the ion cores. Gourary and Adrian\textsuperscript{11} argued that, by orthogonalizing a suitable envelope function to the cores of the lattice...
ions in order to allow for the Pauli principle, the spin density on a nuclear position \((a)\) may be written as a proportionality constant \((A_a)\) times the density of the envelope function on that nucleus. If the envelope wavefunction remains approximately constant within each ion core, a considerable simplification can be achieved. For this situation, Guoruary and Adrian showed that the value of \(A_a\) will only depend on the nuclear species of ion \(a\) and not on its position in the lattice.

This correction has important relevance in magnetic resonance calculations. The proportionality constant \((A_a)\), also known as the “core factor” or the “amplification factor”, must be included in calculation of hyperfine interaction using EMT. For the case of shallow donors, the envelope wavefunction is strongly delocalized. Hence, the core factor is dependent only on the nuclear isotope and not on its position in the lattice. The experimental evidence for validity of this approach has been shown in several magnetic resonance studies\(^{12, 13}\).

### 2.2 Zinc-Blende Crystal Structure

Except for nitrides (such as GaN, AlN which are stable in the wurzite structure), all III-V semiconductors crystallize in zinc-blende structure. A zinc-blende structure has tetrahedral symmetry, i.e. each atom is surrounded by four equidistant nearest neighbours which lie at the corners of a tetrahedron. Zinc-blende structure can be considered to be comprising of two interpenetrating face-centered cubic lattice of same dimensions, one for the cation and the other for the anion. The two cubic lattices are displaced along the body diagonal by one quarter of that body diagonal. This is shown in fig. 2.2.

From the symmetry perspective, due to the presence of two distinct atoms in the Bravais lattice, the zinc-blende structure corresponds to the \(T_d\) (tetrahedral) symmetry point group. Hence the lattice lacks inversion symmetry. The inversion asymmetry of the lattice lifts degeneracy of conduction band corresponding to spin \(\uparrow\) and \(\downarrow\) resulting in many interesting phenomena in these semiconductors such as current and strain induced spin polarization, spin dependent scattering etc. Inversion asymmetry and its consequences are discussed in detail in the next section.
2.3 Inversion Asymmetry

The spin degeneracy of electron states in a solid stems from the simultaneous time-reversal and space-inversion symmetry. The latter requires $E_+(k) = E_+(-k)$ while the first symmetry operation inverts both propagation direction and spin, leading to Kramer’s degeneracy $E_+(k) = E_-(k)$. Here the index $\pm$ denotes the spin state for a given quantization axis. The combined effect of both symmetries yields the spin degeneracy of single particle energies, $E_+(k) = E_-(k)$. Thus, a magnetic field which removes time-reversal symmetry or any potential that breaks space – inversion symmetry may lift spin degeneracy.

In semiconductors with zinc-blende crystal structure (such as GaAs and InP) which lack a centre of space inversion, the corresponding crystal field leads to a bulk inversion asymmetry (BIA). In 2D QWs and heterostructures, the potential which confines the electron in one spatial direction may lead to a structure inversion asymmetry (SIA). The effect of such asymmetry potentials on the electron spin is given by the Pauli term (Eqn. 2.11) and was calculated by Dresselhaus (for BIA) and Bychkov and Rashba\textsuperscript{14,15} (for SIA).

$$H_{so} = -\frac{\hbar}{4m_e c^2} \sigma \cdot (p \times \nabla V(r)) \quad (2.11)$$
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Here $\hbar$ is the Planck’s constant, $m_0$ the bare mass of the electron, $c$ the velocity of light and $\sigma$ the vector of Pauli matrices. $V(r)$ is the electrostatic potential in which the electron propagates with momentum $p$. Since in the context of this dissertation, we are concerned only with bulk semiconductors, we restrict ourselves to the description of Dresselhaus SO terms for Bulk Inversion Asymmetry (BIA).

The spin orbit interaction described by eqn. 2.11 gives rise to zero-magnetic field splitting away from $k=0$ when there is an inversion asymmetry. Such spin splitting can be described as $\hbar\Omega(k) \cdot s$ where $\Omega(k)$ is the precession vector specifying the magnitude of the spin splitting and the direction of the quantization axis. $\Omega(k)$ can be regarded as an effective internal magnetic field $B_{\text{int}}$ that depends on $k$, and is odd in $k$, i.e. $\Omega(k) = -\Omega(-k)$ as a result of Kramer’s degeneracy.

The form of $\Omega(k)$ can be found by symmetry considerations, also known as method as invariants\textsuperscript{16,17}. In the case of bulk inversion asymmetry in zinc-blende crystals\textsuperscript{16},

$$\Omega(k) \cdot \sigma \propto k_x (k_y^2 - k_z^2)\sigma_x + k_y (k_z^2 - k_x^2)\sigma_y + k_z (k_x^2 - k_y^2)\sigma_z$$  \hspace{1cm} (2.12)

This is known as the Dresselhaus spin splitting\textsuperscript{18}. It is to be noted that the effective internal magnetic field ($\Omega(k)$) is always perpendicular to the wave vector ($k$) and is proportional to $k^3$.

In addition to the Dresselhaus splitting, strain induces spin-splitting terms that are linear in the elements of $k$ and the strain tensor $\tilde{\varepsilon}$. The method of invariants leads to two forms of $\Omega(k)$

$$\Omega_3(k) \cdot \sigma \propto (\varepsilon_{yy} - \varepsilon_{zz})k_x \sigma_x + (\varepsilon_{zz} - \varepsilon_{xx})k_y \sigma_y + (\varepsilon_{xx} - \varepsilon_{yy})k_z \sigma_z$$

and

$$\Omega_4(k) \cdot \sigma \propto (\varepsilon_{xx}k_x - \varepsilon_{yx}k_y)\sigma_x + (\varepsilon_{yx}k_y - \varepsilon_{yy}k_z)\sigma_y + (\varepsilon_{yy}k_z - \varepsilon_{zz}k_x)\sigma_z$$

The spin orbit coupling described above opens a possibility of manipulation of electron spins within nonmagnetic semiconductors in absence of applied magnetic field. This has promising implications in the field of spintronics and spin-based quantum information processing. An electrical means of preparing spin-polarized carriers without magnetic materials would provide a step towards all electrical non magnetic spintronic devices. It is clear that current-induced spin polarization can provide that opportunity.
2.4 Current - Induced Spin Polarization

When passing an unpolarised electric current through a SO coupled material, unpolarized electric current is expected to become spin polarized. This was first theoretically proposed in early 90s\textsuperscript{19} and has been explained by several authors since then by using various approaches. A particularly interesting approach\textsuperscript{20} to explain CISP is the one based on equilibrium statistical mechanics for bulk as well as two-dimensional systems. It can be shown that the canonical ensemble average of electrons moving with a wave vector $k$ prescribes a spin polarization antiparallel to the effective magnetic field stemming from the SO coupling (as described in the previous section).

Consider a SO-coupled system subject to the single particle hamiltonian

$$H = \frac{\hbar^2 k^2}{2m} 1 + \mathbf{S} \cdot \mathbf{\omega}(k)$$ (2.13)

where $m$ is the effective mass, $1$ is the $2 \times 2$ identity matrix, $\mathbf{S} = (\hbar/2)\sigma$ is the spin operator, $\sigma$ being the Pauli-matrix vector and $\mathbf{\omega}(k) = (g_e \mu / \hbar) \Omega(k)$ is the momentum dependent Larmor frequency vector, with $\Omega(k)$ being the effective magnetic field stemming from the SO coupling.

For zinc-blende semiconductors, the Larmor frequency in eqn. 2.13 is written as\textsuperscript{21}

$$\mathbf{\omega}(k) = \frac{\eta \hbar^2}{(2m^3 E_g)^{1/2}} \vec{\kappa}$$ (2.14)

where $\eta$ is a dimensionless parameter specifying the spin-orbit coupling strength, $E_g$ is the band gap and $\vec{\kappa}$ is given by:

$$\vec{\kappa} = \begin{pmatrix} k_x(k_y^2 - k_z^2) \\ k_y(k_z^2 - k_x^2) \\ k_z(k_x^2 - k_y^2) \end{pmatrix}$$

When restricted to two-dimension, the component of the wave vector normal to the 2DES is averaged. For [001] quantum wells, one has $k_z^2 \rightarrow \langle k_z^2 \rangle$ and $k_z \rightarrow \langle k_z \rangle = \langle i \hat{z} \rangle = 0$. Thus the Larmor frequency (2.14) takes the form,
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\[ \bar{\omega}^{[001]} = \frac{2\beta}{\hbar} (-k_x, k_y, 0) + \frac{2\beta}{\hbar}(k_x k_y^2 - k_y k_x^2, 0) \]

where \( \beta \) is defined by

\[ \beta = \frac{\hbar^2}{2} \frac{\eta^2}{(2m^* E_g)_{1/2}} \langle k_z^2 \rangle = \frac{\gamma}{\langle k_z^2 \rangle} \]

and is referred to as the Dresselhaus SO coupling constant. The \( \gamma \) parameter is material dependent and is roughly 27eVÅ\(^3\) for both GaAs and InAs\(^2^2\).

In order to derive the equilibrium statistics version of CISP, we write the canonical ensemble average of spin operators of an ensemble of electrons subject to an identical wave vector \( k \) as:

\[ \langle [S]_{k} \rangle = \frac{\hbar}{2} Tr(e^{-\frac{H}{k_B T}}) \sum_{\sigma=\pm} e^{-\frac{E_{\sigma}(k)}{k_B T}} \]

One can show that time–reversal symmetry has two consequences for the Hamiltonian (2.13):

i) \( + \Delta_k = -\Delta_{-k} \) \hspace{1cm} (2.16a)

where \( \Delta_k \) is the spin splitting due to SO coupling.

ii) \( \langle \pm, k | \sigma, \pm, k \rangle = -\langle \mp, k | \sigma, \mp, k \rangle \) \hspace{1cm} (2.16b)

where \( |\sigma, k\rangle \) is the eigenstate of Hamiltonian (2.13)

Using 2.16 and by choosing the basis \( |\sigma, k\rangle \) for the trace, (2.15) can be simplified to

\[ \langle [S]_{k} \rangle = -\frac{\hbar}{2} \tanh \frac{\Delta_k}{k_B T} \Omega(k) \] \hspace{1cm} (2.17)

Following observations from (2.17) are worth noting:

a) In the presence of SO coupling, an ensemble of electrons at rest \( (k \rightarrow 0) \) is unpolarized since \( \Delta_{k \rightarrow 0} = 0 \) while it becomes spin-polarized antiparallel to \( \Omega(k) \) (the effective field) when moving along \( k \).

b) The hyperbolic tangent factor clearly predicts the decrease with \( T \) and increase with \( \Delta_k \) in the polarization magnitude.
Recently, electron spin polarization achieved by current has been demonstrated in semiconductor heterostructures\textsuperscript{23,24,25,26} as well as bulk semiconductors\textsuperscript{27,25}. Since \(\langle k \rangle \propto V\), this implies that the magnitude of CISP defined by (2.17) is expected to increase with the bias. This has been experimentally seen by Kato et al.\textsuperscript{25} in strained GaAs and InGaAs epitaxial layers.

Furthermore, using \(\Delta_k \approx 3.68\text{meV}\textsuperscript{26}\), in (2.17), one can see that CISP may persist up to room temperature:

\[
\left( \frac{\tanh \frac{\Delta_k}{k_B 300K}}{\tanh \frac{\Delta_k}{k_B 10K}} \right) \approx 14\%
\]

CISP has been experimentally observed at room temperature\textsuperscript{28} in n-type ZnSe epilayers. Electrically induced electron spin polarization was imaged using Kerr rotation spectroscopy by Stern et al. at temperatures from 10 to 295K in 1.5\(\mu\text{m}\) thick ZnSe epilayers.

### 2.5 Hot Electron Effect

The “Hot electron” effect was first proposed by G. Feher\textsuperscript{29} in 1959. This effect, also known as the Feher effect, is a nuclear polarization scheme similar to the Overhauser effect (to be discussed in chapter 3) but which does not require an external field to saturate electron spin polarization. It is based on the difference between the electron spin temperature and the temperature corresponding to the mean kinetic energy of the electrons accelerated in a dc electric field.

Consider a system of electrons with \(S=1/2\) coupled to nuclei \(I=1/2\) via the hyperfine interaction \(\vec{A} \cdot \vec{S}\). Let \(W(+ -\leftrightarrow +)\) be the probability that this interaction produces a mutual nuclear-electron spin flip, \(N_+\) the number of electron spins in the \(m_s = \pm 1/2\) states, and \(n_+\) the number of nuclei in \(m_I = \pm 1/2\) states. Assuming that each nuclear flip can proceed only via a simultaneous electron spin flip, one obtains for the steady-state condition

\[
N_+n_+W(+ -\leftrightarrow -+) = N_-n_-W(- +\leftrightarrow ++)
\]

(2.18)

If the nuclei are in thermal equilibrium with the electrons, the ratio of the transition probabilities is

\[
\frac{W(+ -\leftrightarrow -+)}{W(- +\leftrightarrow ++)} = \exp\left(\frac{(\mu_e - \mu_n)B}{kT_H}\right)
\]
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\[ \approx 1 + \left( \frac{\mu_e B}{kT_R} \right) - \left( \frac{\mu_N B}{kT_R} \right) \]

Where \( B \) is the applied magnetic field and \( T_R \) is the temperature of the reservoir that supplies the energy for the simultaneous electron nuclear flip. In the case of conduction electrons it is supplied by their kinetic energy. The electron and nuclear spin population may be characterized by spin temperature \( T_S \) and \( T_N \) defined by the relations:

\[ \frac{N_e}{N_-} = \exp \left( -\frac{\mu_e B}{kT_s} \right) \approx 1 - \frac{\mu_e}{kT_S} \]

And

\[ \frac{n_e}{n_-} = \exp \left( \frac{\mu_N B}{kT_N} \right) \approx 1 + \frac{\mu_N}{kT_N} \]

From these definitions and using equation 2.18, it follows that:

\[ \frac{\mu_N B}{kT_N} = -\frac{\mu_e B}{kT_s} + \frac{\mu_e B}{kT_R} - \frac{\mu_N B}{kT_R} \]

Therefore,

\[ \frac{1}{T_N} = \frac{\mu_e}{\mu_N} \left( \frac{1}{T_R} - \frac{1}{T_S} \right) - \frac{1}{T_R} \quad (2.19) \]

It is seen from the above relation that the nuclei may be polarized along or opposite to the external magnetic field depending on the difference between the electron spin temperature and the temperature corresponding to their mean kinetic energy. In the Overhauser effect it is assumed that \( T_R = T_L \), where \( T_L \) is the lattice temperature and \( T_S > T_L \). The second condition is obtained by saturating the electron spin transitions. In the case of hot electrons \( T_R \) is not equal to \( T_L \) and nuclear polarizations may be attained even without the application of a saturating microwave field.

Measurements of \( T_S \) and \( T_R \) were performed by Feher\(^2\) on Si:P \( (N_D = 2 \times 10^{16} \text{cm}^{-3}) \) at 1.3K. The electrical characteristics of the sample are shown in fig.2.3.
The deviation from Ohm’s law at higher fields is an indication that the electrons are “hot”, i.e. they are not in thermal equilibrium with the lattice. At field strength of about 150V/cm, the sample showed breakdown. Since the breakdown is expected to be the result of impact ionization of the donors by the accelerated electrons, $T_R$ at the breakdown should be close to 500K (corresponding to donor ionization energy: 0.044eV). The spin temperature of the free carriers (obtained by measurement of spin resonance signal) was measured to be about 2.6K. Thus, a sizable difference between $T_R$ and $T_S$ was demonstrated. However, the number of electrons was too small to have produced a nuclear polarization.
2.6 Current-Induced Dynamic Nuclear Polarization

Nuclear polarization by means of the Feher effect was first observed in InSb (n-type, electron concentration: $N_d = 4 \times 10^{15} \text{cm}^{-3}$) by Clark and Feher\textsuperscript{30}. NMR signal enhancement factors of up to 4 and 12 were measured for $^{115}\text{In}$ and $^{123}\text{Sb}$ nuclei respectively under the effect of dc current. The FID signal from $^{115}\text{In}$ nuclei with and without the application of electric field is shown in fig. 2.4.

![Figure 2.4: Effect of dc current on nuclear resonance signal of $^{115}\text{In}$ in InSb at 4.2K. Figure taken from reference [30]](image)

Apart from an enhancement of the nuclear polarization, an enhancement of the nuclear spin lattice relaxation rate was also observed in the presence of a dc electric field. The observed effects of electric field can be explained by the "hot electron theory" proposed by Feher. For the derivation of eqn. 2.19, it was assumed that electron-nuclear hyperfine interaction is the strongest interaction and other interactions were neglected. However, in a more general scenario, one must take into account the possibility of nuclear relaxation via means other than the
conduction electrons. Eqn. 2.19 is thus modified to obtain the enhancement factor as:

\[
\phi = \frac{T_L}{T_N} = \frac{\mu_n}{\mu_N} \left[ \left( \frac{1}{T_R} \frac{1}{T_S} \right) \tau + \frac{T_L}{T_R} \frac{\tau}{\tau_N} + \frac{\tau}{\tau_L} \right]
\]

(2.20)

where \(T_L\) is the lattice temperature, \(T_N\) the nuclear temperature, \(\tau\) is the total nuclear spin lattice time, \(\tau_R\) represents the part of the nuclear relaxation time which proceeds via the conduction electrons, and \(\tau_L\) the nuclear relaxation time for other processes. The ratio \(\tau/\tau_R\) represents a short circuiting effect of the different nuclear relaxation processes.

In case of InSb, \(g_e = -50\) and hence \(\mu_n/\mu_N\) is a negative quantity. Furthermore, for hot electrons, \(T_R > T_S\). Thus, enhancement factor is positive and an increase in NMR signal can be obtained by application of dc electric field. The enhancement factor is higher for Sb as compared to In due to smaller leakage relaxation rate and stronger hyperfine interaction of Sb nuclei.

The enhancement of the nuclear spin lattice relaxation rate can be explained by including the contribution of paramagnetic impurities. It is well known that all semiconductors include some paramagnetic impurities. Moreover, in n-type semiconductors, an electron localized on a donor atom also acts as a paramagnetic centre. The conduction electrons and localized electrons in such a system reach thermal equilibrium through rapid exchange processes on a time scale \(\sim 10\text{ps}^{31}\). Thus, the spin polarized "hot electrons" are in equilibrium with paramagnetic centres which in turn play an important role in nuclear relaxation (via spin diffusion).

This unique method of enhancing nuclear polarization did not receive any attention since its prediction and initial observation in 1963. However, recent proposals\(^{32,33,34,35}\) for application of highly polarized nuclei in spintronics and quantum computing have led to a renewed interest in the possibility of enhancing nuclear polarization by application of dc electric field.
Chapter 3

Magnetic Resonance: Experimental Techniques, Basic Principles

This chapter outlines the theoretical concepts and experimental techniques pertinent to the understanding of this dissertation. A brief description of basic principles and working of magnetic resonance techniques such as Nuclear Magnetic Resonance, Electron Spin Resonance, Overhauser shift spectroscopy is outlined. Special relevance of these techniques to the study of semiconductors is highlighted. Concepts such as hyperfine interaction, spin diffusion, Overhauser effect are essential to understand dynamic nuclear polarization in semiconductors. They are described in this chapter in detail in order to set a foundation for the chapters to follow.

3.1 Nuclear Magnetic Resonance Spectroscopy

Nuclear Magnetic Resonance (NMR) experiments probe the properties of atomic nuclei and their local environment by recording the transitions between nuclear spin energy levels. The energy separation is determined primarily by the Zeeman interaction, which varies linearly with the strength of the applied magnetic field $B_0$. This is shown in fig. 3.1. The
magnitude of the Zeeman splitting for a given value of $B_0$ primarily depends on the nucleus. However, it is modified by the local environment of the nucleus such as due to coupling to nearby electrons or nuclear spins and the orientation dependent coupling to an electric field gradient (quadrupolar coupling for $I>1/2$). Since NMR is capable of providing information about diverse set of observables, it is a premier spectroscopic tool for chemical and structural analysis at the atomic level.

\[ \begin{align*}
&+\frac{\Delta E}{2} \\
&0 \\
&-\frac{\Delta E}{2}
\end{align*} \]

Zeeman Energy

\[ \begin{align*}
&m = -1/2 \\
&m = +1/2
\end{align*} \]

Magnetic Field ($B_0$)

Fig. 3.1: Zeeman energy splitting of nuclear spin states for $I=1/2$ nucleus.

The most important components of a basic NMR experimental set up comprises a source of strong and homogenous magnetic field and a coil around the sample (with axis orthogonal to $B_0$) which serves as the source of radiofrequency irradiation used to induce NMR transitions. An oscillating voltage applied across the coil circuit at angular frequency $\omega$ provides a magnetic field with amplitude $2B_1$ directed orthogonal to $B_0$ and with the angular frequency $\omega$. When the irradiation frequency matches the nuclear larmor frequency given by:

\[ \omega_0 = \frac{\Delta E}{\hbar} = -\gamma B_0 \]

where $\hbar$ is Planck’s constant divided by $2\pi$ and $\gamma$ is the nuclear gyromagnetic ratio, it induces transitions between Zeeman energy levels. In modern NMR spectroscopy, simple absorption or emission measurements in the frequency domain are replaced by a time-domain experiment where broadband RF pulses excite coherent spin transitions and subsequent time evolution of the magnetic moment $\mathbf{M}$. Thermal populations of the spin $1/2$ Zeeman levels exhibit net alignment of nuclear magnetic moments along $B_0$ yielding a corresponding sample magnetization,

\[ \mathbf{M} = N\gamma h\langle \mathbf{I} \rangle \]

in the same direction, where $N$ is the number of spins in the ensemble and $\mathbf{I}$ is the nuclear spin angular momentum operator. A short resonant
RF pulse turns $\mathbf{M}$ away from $B_0$. In the case where pulse duration $t_p$ is such that,

$$\gamma_n B_0 t_p = \frac{\pi}{2}$$

this rotation is by 90° and places $\mathbf{M}$ in the transverse plane. Following this $\frac{\pi}{2}$ pulse, $\mathbf{M}$ precesses about $B_0$. (Shown in fig. 3.2)

![Fig 3.2: Nuclear magnetic moment $\mathbf{M}$ resulting from net alignment of spins along $B_0$ and precession of $\mathbf{M}$ about $B_0$ following a $\pi/2$ pulse.](image)

This precession induces a voltage proportional to $\frac{d}{dt}\mathbf{M}$ in a nearby coil. The signal voltage is given by:

$$S(t) = A \cos(\omega_0 t) e^{-\frac{t}{2T_2}}$$

where $A$ is a scaling factor proportional to $M$, $\omega_0 = \Delta E/\hbar$ is the nuclear Larmor frequency and $T_2$ is the transverse nuclear spin relaxation constant as described in the next section. The Fourier transform of time-domain signal $S(t)$ results in a single Lorentzian peak at $\omega_0 = \Delta E/\hbar$ in frequency domain and with a full width at half max (FWHM) of $(\pi T_2)^{-1}$. This is shown in fig. 3.3.
Longitudinal relaxation time

At equilibrium, the net magnetization vector ($\mathbf{M}$) lies along the direction of the applied magnetic field $B_0$. In this configuration, the $z$ component of magnetization $M_z$ equals $\mathbf{M}$. $M_z$ is referred to as the longitudinal magnetization. Rotation of magnetization direction by means of a 90° pulse places $\mathbf{M}$ in the transverse plane. In this situation $M_z = 0$. The time constant which describes how $M_z$ returns to its equilibrium value is called the longitudinal relaxation time ($T_1$). The equation governing this behaviour as a function of the time $t$ after its displacement is:

$$M_z = M_0(1 - e^{-\frac{t}{T_1}})$$

where $M_0$ is the magnitude of equilibrium magnetization. The longitudinal relaxation time ($T_1$) is essentially the time the spins need to exchange energy with the surrounding thermal reservoir or lattice. Hence, it is also known as the nuclear spin lattice relaxation time. The two most commonly used pulse sequences for measurement of nuclear spin lattice relaxation time are:

- Saturation recovery
- Inversion recovery

Transverse relaxation time

When the net magnetization is placed in the $xy$ plane, it rotates about the $z$ axis at Larmor frequency. In addition to the rotation, the net magnetization starts to dephase because each of the spin packets comprising it experiences a slightly different magnetic field and rotates at its own Larmor frequency. The longer the elapsed time, the greater is the phase difference. The time constant at which the transverse magnetization returns to equilibrium is defined as the transverse relaxation time. Since the dephasing of spins is mainly due to the
interactions with neighboring spins, the transverse relaxation time is also known as the nuclear spin-spin relaxation time. Two factors which contribute to the decay of transverse magnetization are:

- molecular interactions resulting in pure $T_2$ molecular effect
- variations in $B_0$ leading to inhomogeneous $T_2$ effect

The combined time constant due to these two effects is called $T_2^*$ and is given by:

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_{2\text{inhomo}}}$$

### 3.1.1. NMR in Semiconductors

Nuclear magnetic resonance is a highly local measurement technique and has been used extensively for the study of semiconductors. NMR is well suited to study semiconductors because the NMR parameters (resonance frequencies, linewidths, lineshapes, and spin lattice relaxation rates) are determined primarily by two types of interactions:

- Hyperfine interaction with conduction band electrons or electrons localized on dopants/impurities.
- Quadrupolar interaction with electric field gradients close to impurities or dislocations.

As described in section 2.1, localized electrons in semiconductors have extended wavefunctions. As a result, nuclei close to these localized electrons experience strong hyperfine interaction leading to interesting effects such as the shift of the NMR line positions (paramagnetic shift or the Knight shift), shift of the ESR frequency (Overhauser shift), nuclear spin lattice relaxation by means of HFI with the conduction electrons or the donor electrons and enhancement of nuclear spin polarization (dynamic nuclear polarization or the Overhauser effect). These effects are explained in detail in the following sections. The point of interest here is that due to strong coupling of nuclei with the localized electrons, magnetic nuclei can be used to investigate the distribution and polarization of conduction electrons in semiconductors by using hyperfine interaction as a local probe at the site of the nucleus. Since hyperfine interaction strongly depends on the degree of localization of electrons, measurements of $T_1$, Knight shift and DNP can provide useful information about the type of electrons (itinerant or localized) responsible for these effects.

Moreover, most of the nuclei in semiconductors, especially III-V semiconductors ($^{71}\text{Ga}$, $^{69}\text{Ga}$, $^{75}\text{As}$, $^{115}\text{In}$) have $I>1/2$ and hence have non-zero quadrupolar moment. Any deviations from perfect cubic symmetry
and presence of defects in the crystal lattice, thus, results in quadrupolar splitting and quadrupolar relaxation. This can be exploited to investigate the presence of impurities, electric field gradients and various other strain-induced-effects in these semiconductors. Guerrier et al.\textsuperscript{36} measured quadrupolar splitting of nuclear magnetic resonances induced by application of external strain to lattice matched GaAs/AlGaAs quantum well. Such calibration of quadrupolar splitting versus applied strain provides a basis for a measurement of built-in strain in strained layer heterostructures\textsuperscript{37}.

Since NMR parameters in semiconductors are very sensitive to the electron concentration, extensive NMR studies on semiconductors have been performed for investigation of metal-insulator-transition\textsuperscript{38}. For example Knight shift measurements have been used to study metal insulator transitions\textsuperscript{39,40}.

In quantum wells, quantum dots and other semiconductor heterostructures, the electronic wavefunction is modified by confinement. The situation is similar to an electron localized on a donor/impurity resulting in strong hyperfine interactions close to the electrons. Since the Knight shift is proportional to the square of the wave function, it has been proposed to use Knight shift studies to determine the excited state electron wavefunction of a quantum well\textsuperscript{41,42,43}. Several indirect measurements of spin polarization of 2D electrons in quantum wells have been performed by measuring Knight shift of NMR lines which is a direct measure of the additional local effective magnetic field created by the electronic spins at the position of the nucleus\textsuperscript{44}.

3.2 Electron Spin Resonance Spectroscopy

Electron Spin Resonance (ESR) spectroscopy is a well known technique used for measurement of electron spin polarization analogous to the Nuclear magnetic resonance used for nuclei. An unpaired electron spin has a magnetic moment associated with it which is given by:

$$\mu = \gamma S = -g \frac{\mu_B}{\hbar} S$$

Here $\gamma$ denotes the magnetogyric ratio which is expressed in terms of $g$ factor, Bohr magneton ($\mu_B$) and $\hbar$ which is the Planck constant divided by $2\pi$. In the presence of an external magnetic field $\mathbf{B}$, the magnetic moment $\mu$ has the energy $E = -\mu \cdot \mathbf{B}$, which leads to the Hamiltonian of the Zeeman interaction

$$\hat{H} = g \frac{\mu_B}{\hbar} \mathbf{B} \cdot \mathbf{S}$$
When the Cartesian z axis points along the direction of magnetic field, only the $S_z$ component of the spin is relevant. Using the Eigen value relation $S_z|\phi\rangle = \hbar m_s|\phi\rangle$, we obtain the quantized energy levels:

$$E = g\mu_B B m_s$$

The energy values are determined by the magnetic quantum number $m_s = -S, \ldots, S-1, S$ resulting in $2S+1$ energy levels. The energy difference between these levels corresponds to frequencies in the GHz range for magnetic fields from a few millitesla to several Tesla. Microwave in the appropriate frequency range can thus be used to induce transitions between electronic Zeeman levels. The selection rule $\Delta m_s = \pm 1$ leads to the ESR resonance condition given by:

$$\hbar \nu = \Delta E = g\mu_B B$$

where $\nu$ is the transition frequency and $\hbar$ the Planck constant. For the free electron, the $g$ value is $g_e=2.0023$. This value can however be modified by spin orbit interactions in atoms, molecules and solids.

### 3.2.1 ESR in semiconductors

Any system with unpaired electrons offers a possibility to observe electron spin resonance in principle. In case of intrinsic semiconductors, the only unpaired electron system present is that of the conduction electrons. However, practical difficulties such as the relatively small number of conduction electrons and short spin-lattice relaxation times may make the observation of ESR difficult in such systems. The extrinsic semiconductors where ESR is observed easily can be divided into following categories:

- semiconductors with ‘shallow’ donors and acceptor impurities
- semiconductors with ‘deep’ impurities
- semiconductors with conduction electrons
- semiconductors with radiation damage centres
- semiconductors with surface states

For the present study, we shall concentrate on ESR on shallow donors in III-V semiconductors.

Group II impurity atoms enter the crystal lattice of III-V semiconductors by substitution, replacing the group III host atoms and the group VI impurity atoms replace group V host atoms forming acceptor and donor centres respectively. Group III-V compounds have not yet been prepared to the same degree of purity as silicon and germanium. The residual impurities introduced during the crystal –growth process can thus not be avoided. It is known that bulk samples of InP include silicon and/or sulphur impurities at a concentration of about $10^{15}$/cm$^3$. Bulk samples of GaAs include residual impurities of Si and C at concentration of about $10^{14}$/cm$^3$. 

Using the effective mass theory as described in section 2.1, radii of the ‘1s-like’ orbits of shallow donors can be determined. Since the electron effective masses for donors in III-V semiconductors are very small (in the range 0.013\(m_0\) to 0.07\(m_0\)), the radii of the shallow donor impurity states are very large (8nm to 64nm). This leads to an overlap of donor wave functions and creation of impurity bands. Depending upon the concentration of donors, the donor wave functions have varying degrees of overlap, leading to partial, complete or no delocalization of donor electrons. The three possible scenarios are as follows:

(i) Very low doping concentration (<10^{14}/cm^3)

For such low doping concentrations, donor electrons are non-interacting and follow Boltzmann statistics. The donor wave functions do not overlap at such low concentrations and thus the electron spin is completely localized at the donor atom position. Since the donor wave function is extended over a large number of nuclei, the hyperfine interaction experienced by nuclei has a distribution. This results in a broadened gaussian ESR line where only hyperfine-structure of the central core is resolved. Such systems can be studied by means of Electron-Nuclear Double Resonance technique (ENDOR).

(ii) Intermediate doping concentration

For a higher doping concentration, the donor wave functions start to overlap and impurity bands are created. The donor electrons are thus partially delocalized leading to lorentzian shaped motional and exchange narrowed ESR lines. The hyperfine interaction is still position dependent. However, hyperfine structure is not resolved and cannot be studied by ENDOR anymore. Overhauser shift spectroscopy is a suitable technique for study of such systems.

(iii) High doping concentration (>MIT)

Beyond the metal-insulator transition, the donor electrons are completely delocalized. Electrons follow Fermi-Dirac statistics leading to Pauli-paramagnetism.

### 3.3 Hyperfine Interaction

The Hamiltonian operator for hyperfine interaction between and electron spin \(S\) and a nuclear spin \(I\) is written as:

\[
\hat{H}_{HF} = \hat{I} A \hat{S}
\]  

(3.1)

If the magnetic field \(B_\theta\) is considered to be along \(z\) direction of the principle axis system of hyperfine tensor, only the diagonal elements of the tensor remain and one may write:

\[
\hat{H}_{HF} = A_{xx} \hat{I}_x \cdot \hat{S}_x + A_{yy} \hat{I}_y \cdot \hat{S}_y + A_{zz} \hat{I}_z \cdot \hat{S}_z
\]  

(3.2)
If the external magnetic field $B_0$ is sufficiently large such that $|g\mu_B B_0| \gg A_{zz}$, the term $A_{zz} \cdot \hat{I}_z \cdot \hat{S}_z$ does not induce any transition in $m_I, m_S$. The energy levels are however shifted. Using the operators for $\hat{I}_+^+ (I_z = \hat{I}_z \pm i \hat{I}_y)$ (similarly for $\hat{S}_+^+$ and $\hat{S}_-$) one may write

$$\hat{H}_{\text{HF}} = \frac{1}{4} (A_{xx} + A_{yy}) (I_+^+ S^-_+ + I_-^+ S^+_+ + I_-^+ S^+_+ + I_+^+ S^-_+ + I_-^- S^+_+ + I_+^- S^-_+)$$  \hspace{1cm} (3.3)

- The first term of eqn. 3.3 drives a transition $\Delta m_I = \pm 1$ and $\Delta m_S = \mp 1$ and is called flip-flop transition.
- The second term drives a transition with $\Delta m_I = \pm 1$ and $\Delta m_S = \pm 1$ and is called the flip flip transition.

In case when $A_{xx} = A_{yy} = A_{zz}$, the hyperfine interaction is scalar and the tensor $A$ can be represented by a hyperfine constant ($A$). Flip–flip processes do not occur in such a case. This scenario is found in systems with cubic crystal structure. In case of an axial symmetry, $A_{xx} = A_{yy} \neq A_{zz}$. Here also only flip-flop processes occur.

The hyperfine interaction between electron and nuclear spins is known to transfer polarization from one spin system to the other in the presence of a longitudinal magnetic field. Especially in the case when one spin system is strongly out of equilibrium, the other can be polarized very efficiently. This is the basic working principle behind optical pumping experiments where a strong non equilibrium situation is created by generating a steady state electron spin polarization. Under suitable conditions, this non equilibrium situation leads to a strong polarization of the nuclear spin system. There are two types of hyperfine interaction: the dipolar hyperfine interaction and the contact (or scalar) hyperfine interaction.

**Dipolar Hyperfine Interaction**

The dipolar hyperfine interaction is an interaction between the magnetic moments of the electron and the nuclear spin in analogy to the classical dipolar interaction between magnetic moments. As long as the nuclear and electron moments $\mu_e$ and $\mu_n$ are far apart, their interaction is expected to be that of a pair of magnetic dipoles, the Hamiltonian being

$$\hat{H} = \frac{\mu_e \cdot \mu_n}{r^3} - \frac{3(\mu_e \cdot r)(\mu_n \cdot r)}{r^5}$$  \hspace{1cm} (3.4)

where $r$ is the radius vector from the nucleus to the electron.
Contact Hyperfine Interaction

If the electronic wave function is a $p$-state, $d$-state, or other state of non zero angular momentum, eqn. 3.4 is a good approximation. For $s$-states however, the electron wave function is non zero at the nucleus and the dipolar approximation breaks down. In this situation, the contact hyperfine interaction becomes important. The Hamiltonian of this interaction is given by

$$\hat{H} = \hat{I} A_{fc} \hat{S}$$

Where $A_{fc}$ is the Fermi Contact Hyperfine constant given by:

$$A_{fc} = \left( \frac{8\pi}{3} \frac{\hbar}{4\pi} \right) \left( \frac{\mu_e}{4\pi} \hbar \gamma \right) \left| \psi(r) \right|^2$$

(3.5)

$\psi(r)$ being the electron wavefunction at the nucleus site.

Since $A_{fc}$ is proportional to the electron wavefunction at the nuclear site, the measurement of $A_{fc}$ provides a possibility of wavefunction determination. The dipole-dipole interaction of the magnetic moments, introduces an anisotropy element in the Hyperfine interaction.

3.3.1: Hyperfine Interaction in Semiconductors

The Hyperfine interaction is a dominant interaction existing in most semiconductors. The presence of this interaction makes double resonance possible in semiconductors and is responsible for several interesting phenomena/effects such as

- Shift of the NMR line positions (known as the paramagnetic shift or the Knight shift). The shift is proportional to $A \cdot \langle S_z \rangle$ where $\langle S_z \rangle$ is the average $z$ component of the electron spin polarization.

- Shift of the ESR frequency, known as the Overhauser shift. The shift is proportional to $A \cdot \langle I_z \rangle$ where $\langle I_z \rangle$ denotes the average nuclear spin polarization.

- Nuclear spin lattice relaxation mechanism is dominated by HFI for nuclei strongly coupled either to the conduction electrons or the donor electrons.

- Saturation of ESR transition leads to an enhancement of nuclear spin polarization. This phenomenon is known as dynamic nuclear polarization (DNP) or the Overhauser effect.

In most semiconductors, such as GaAs, the conduction states near the $\Gamma$ point have $s$-like character. Hence for the conduction electrons, the
contact hyperfine interaction dominates. In the valence band, the states have a p-like character which causes the contact hyperfine interaction to be negligible. In such cases dipolar hyperfine interaction dominates. However, in proximity to the localized electrons, the dipolar hyperfine interaction is strongly affected by contact hyperfine interaction. It has been shown that in semiconductors like GaAs where the Bohr radius is large, the Fermi contact hyperfine interaction is much stronger than the dipolar interaction wherever the square of the electron wavefunction is not negligible\(^45\). Thus, the concentration of localized electrons (and hence the distance between them) governs which type of hyperfine interaction dominates in semiconductors. For example, a recent study on \(n\)-doped and semi-insulating GaAs has demonstrated that the Fermi contact term is 1000 times stronger than the dipolar term\(^46\) when the distance between impurities is less than 50nm.

### 3.4 Dynamic Nuclear Polarization

In the last few years dynamic nuclear polarization has received increased attention by the EPR, NMR and microwave engineering community. Several DNP strategies have been proposed and used successfully to enhance sensitivity in a wide range of NMR, imaging as well as in vivo applications in the medical MRI field. Optical pumping and subsequent DNP is being extensively used as a preferred signal enhancement technique in semiconductors. Study of DNP also provides information such as the magnitude of interaction between electron and nuclei, electron exchange and electronic and nuclear relaxation. Since major part of this dissertation deals with dynamic nuclear polarization, a detailed theoretical explanation of this effect and its relevance in semiconductors is presented in this section.

In a system of two types of interacting spins I and S in a static magnetic field \(B_0\), the polarization of I depends on polarization of S. Any deviation of equilibrium population of Zeeman levels of S has a tendency to produce a polarization of I. This is termed as dynamic nuclear polarization. This process originates from relaxation processes involving both the spins S and I. It was first predicted by Overhauser\(^47\) and is often referred to as the "Overhauser effect". A different type of DNP is produced by a simultaneous flip of one spin I and one spin S when absorbing quanta of the energy \(\hbar(\omega_i \pm \omega_s)\) from the radio frequency field. These transitions are forbidden but become weakly allowed if the corresponding spin states are mixed by an interaction between the spins. Since this effect occurs mainly in solids, it is termed as "solid state effect".
### 3.4.1 Overhauser Effect

In order to understand the basic concept of Overhauser effect let us consider a simple system where a nuclear spin (I=1/2) is coupled to an electron spin (S=1/2), acted on by an external magnetic field \( B \). The Hamiltonian for the system is given by:

\[
\hat{H} = \gamma_e \hbar B \hat{S}_z + A \hat{I} \cdot \hat{S} - \gamma_n \hbar B \hat{I}_z
\]

where the first term represents the interaction of electron with external magnetic field, the second term is the Hyperfine contact interaction (form of electron-nuclear coupling appropriate for s-states) and the last term represents the interaction of nuclear spin with the external magnetic field. In the weak coupling regime (or the strong field approximation), \( A \ll \gamma_e \hbar B \), the energy eigenvalues of the Hamiltonian are:

\[
E = \gamma_e \hbar B m_s + Am_I m_s - \gamma_n \hbar B m_I
\]

\[
m_s = \pm \frac{1}{2}, m_I = \pm \frac{1}{2}
\]

The eigen states are given by \(|-\rangle, |-\rangle, |+\rangle\) and \(|+\rangle \) where + and − refer to the state of the electron and nucleus respectively. An eigen state with \( m_s = \frac{1}{2} \) and \( m_I = -\frac{1}{2} \) is written as \(|+\rangle \).

The selection rules for transitions induced by an applied alternating field are:

\[
\Delta m_s = \pm 1, \Delta m_I = 0 \quad \text{or} \quad \Delta m_I = \pm 1, \Delta m_s = 0
\]

The first corresponds to an electron spin resonance and the second to nuclear resonance. Their resonance frequencies \( \omega_e \) and \( \omega_n \) are:

\[
\omega_e = \gamma_e B + \frac{Am_I}{\hbar} \quad \text{and} \quad \omega_n = \gamma_n B - \frac{Am_s}{\hbar}
\]

Thus, there are four allowed transitions. These are shown in Fig.3.4. The diagram is drawn for the case \( \gamma_s > 0 \) and \( A \ll \gamma_e \hbar B \). The ESR and the NMR transitions are shown with resonance frequencies \( \omega_e \) and \( \omega_n \) respectively. The transition involving simultaneous spin flip of electron and nuclear spins in opposite directions (0 quantum transition) is shown as dotted line.
Fig. 3.4: Energy level diagram for a coupled electron-nuclear spin system. The ESR and NMR transitions are shown in solid lines. Simultaneous spin-flip transition is shown in dotted line.

Fig. 3.5(a) shows the thermal equilibrium population distribution for the coupled electron-nuclear spin system. If such a system in thermal equilibrium is perturbed by microwave excitation of the two ESR transitions (solid arrows) and if the ESR transition rate exceeds the electron spin relaxation rate, then the ESR transition will be saturated. This is shown in Fig. 3.5(b). If the electron spin system relaxes via simultaneous electron-nuclear spin transition (for example via hyperfine interaction), the net effect is the enhancement of nuclear spin polarization as seen in fig. 3.5(c). Thus, the net effect of ESR saturation is to convert the electron polarization that existed at thermal equilibrium to nuclear polarization. Thermal equilibrium nuclear polarization is:

$$\langle \hat{I}_Z \rangle_0 = \frac{1}{2} \frac{\gamma_e h B}{2kT}$$

Whereas the steady state nuclear polarization can be written as:

$$\langle \hat{I}_Z \rangle = \frac{1}{2} \frac{\gamma_e h B}{2kT}$$

This corresponds to an enhancement of nuclear polarization equal to:

$$\frac{\langle \hat{I}_Z \rangle}{\langle \hat{I}_Z \rangle_0} = \frac{\gamma_e}{\gamma_n}$$

This enhancement is obtained for complete saturation of electronic transitions. Enhancement of nuclear polarization is however possible even with any perturbation of the electron system from thermal equilibrium. A general expression for enhancement of nuclear polarization is written as:

$$\frac{\langle \hat{I}_Z \rangle}{\langle \hat{I}_Z \rangle_0} = s \frac{\gamma_e}{\gamma_n}$$
where $s$ is the ESR saturation factor, $0<s<1$. ($s=1$ for complete ESR saturation).

Fig. 3.5 Energy level diagram and population distribution of a coupled electron-nuclear spin system (a) in thermal equilibrium (b) under microwave saturation and (c) after electron-nuclear spin flip.
A more quantitative derivation of nuclear enhancement factor is given below:

Consider the interaction of an electronic spin system $S=1/2$ ($E_+ > E_-$) with nuclear system. The nuclear spin system is in a state of thermal equilibrium and so the probability $P_f$ of occurrence of state $f$ is proportional to $\exp (-E_f / kT)$.

The nuclei induce transition in the spin system from + to – with the probability $W_{+-}$ and vice versa. Thus we have:

$$\frac{W_{+-}}{W_{-+}} = \exp\left( \frac{E_+ - E_-}{kT} \right)$$  \hspace{1cm} (3.6)

Due to the coupling between electron and the nuclear system, the transition rate from high to low energy level is enhanced. This asymmetry of the transition rates facilitates dynamic nuclear polarization. The coupling of electron and the nuclear system can now be introduced under the following conditions:

- The HFI is only scalar
- $S=I=1/2$
- the nuclear spin flip is always accompanied by an electron spin flip

Under thermal equilibrium we must have,

$$N_+ n_+ W_{(+)(-)} = N_- n_- W_{(-)(+)}$$  \hspace{1cm} (3.7)

And using eqn. 3.6 we have,

$$\frac{W_{(+)(-)}}{W_{(-)(+)} } = \exp\left( \frac{E_+ - E_-}{kT} \right)$$  \hspace{1cm} (3.8)

The energies $E_+$ and $E_-$ can be written as a sum of electron and nuclear Zeeman terms and the HFI for the antiparallel spin settings for the two. On taking the difference, the HFI energy cancels and from eqn. 3.8 we have,

$$\frac{W_{(+)(-)}}{W_{(-)(+)} } = \exp\left( \frac{\hbar(\omega_s - \omega_i)}{kT} \right)$$  \hspace{1cm} (3.9)

where, $\omega_s = -\gamma_s B_0$ and $\omega_i = -\gamma_i B_0$

By saturating electronic transition by means of radiation at frequency $\omega_s$, in eqn. 3.7, $N_+ = N$. and from 3.9 we have,

$$\frac{n_+}{n_-} = \exp\left( \frac{\hbar(\omega_s - \omega_i)}{kT} \right)$$  \hspace{1cm} (3.10)

In thermal equilibrium the nuclear polarization is given by:

$$\exp\left( \frac{\hbar(-\omega_i)}{kT} \right)$$
From eqn. 3.10 it is clear that the nuclear polarization is enhanced by a factor:

\[
\frac{\omega_s - \omega_i}{\omega_i} \approx \frac{\gamma_s}{\gamma_i}
\]  

(3.11)

This enhancement of nuclear spin polarization is known as the Overhauser effect. This mechanism of dynamic nuclear polarization exists in situations where a rapid relative electron-nucleus motion exists in the sample (such as for paramagnetic impurities in liquids and conduction electrons in metals). Dynamic nuclear polarization in samples where the electron spins have fixed positions in space occurs via a different mechanism. This is dealt with in the next section.

### 3.4.2 Solid State Effect

The explanation of Overhauser effect was based on an assumption that the electron nuclear interaction is purely scalar \(I.S\) coupling. If the interaction is not purely scalar, extra transition probabilities such as \(W_{(\pm)\rightarrow(\pm)}\) and \(W_{(\pm)\rightarrow(\mp)}\) also occur and their contribution must be added on both sides of eqn.3.7. Let us consider a situation where the energy required for a simultaneous flip (such as \(W_{(+)}\rightarrow(-)\) or \(W_{(+)}\rightarrow(-)\)) is provided by an external RF source at the frequency

\[\Omega = \omega_s + \omega_i \text{ or } \Omega = \omega_s - \omega_i\]

We assume that the intensity of the source at frequency \(\Omega\) is such that the corresponding rate of transitions is much faster than the nuclear relaxation rate \((1/T_1)_i\) but much slower than the electronic rate \((1/T_1)_s\). Thus the electronic populations will be practically unaffected by the radio-frequency and will keep their Boltzman equilibrium values. However, the nuclear populations will be given by the relations:

\[
\frac{n_+}{n_-} = \left(\frac{N_+}{N_-}\right)_0 = \exp(-\frac{\hbar\omega_s}{kT}) \text{ if } \Omega = \omega_s - \omega_i
\]

\[
\frac{n_+}{n_-} = \left(\frac{N_+}{N_-}\right)_0 = \exp(\frac{\hbar\omega_s}{kT}) \text{ if } \Omega = \omega_s + \omega_i
\]

resulting in enhancement factors given by:

\[
\frac{\omega_s}{\omega_i} = \frac{\gamma_s}{\gamma_i} \text{ if } \Omega = \omega_s + \omega_i
\]

\[
\frac{\omega_s}{\omega_i} = -\frac{\gamma_s}{\gamma_i} \text{ if } \Omega = \omega_s - \omega_i
\]

This mechanism of dynamic nuclear polarization is termed as the "solid-state effect".
3.4.3. DNP Mechanism in Semiconductors

The existence of the two above mentioned mechanisms of dynamic nuclear polarization depends strongly on the extent of localization of the electron spins. In samples where electrons are completely delocalized (such as the paramagnetic impurities in liquids and conduction electrons in metals), DNP occurs via the Overhauser effect. When electron spins have fixed positions in space, the solid state effect is more dominant. This is commonly seen in the case of solid samples with paramagnetic impurities. In semiconductors, the dominant mechanism of dynamic nuclear polarization depends critically on the concentration of donor electrons. Phosphorus-doped silicon is the best example to illustrate this dependence. For small concentrations of phosphorus atoms (<5 × 10^16 cm\(^{-3}\)), the ESR spectrum shows a hyperfine split line with a separation of about 40 Gauss\(^{48,49}\). At such low doping concentrations, the solid-state effect dominates the dynamic nuclear polarization. As the doping concentration is increased, a third line appears half-way between the hyperfine split lines. This third line originates from the exchange coupled clusters in which exchange energy is much larger than the donor hyperfine interaction\(^ {50,49}\). This central line grows at the expense of the other two lines with increasing doping concentration. Finally at concentrations close to 10^18 cm\(^{-3}\), the ESR spectrum shows a single line. Such heavily doped samples with a single electron resonance line show the Overhauser effect rather than the solid state effect\(^ {51,38}\).

Similar exchange narrowed ESR lines are observed in undoped InP samples leading to huge Overhauser enhancement factors. This is discussed in detail in chapter 5. Since the electron resonance line is considerably narrowed by strong exchange coupling between the electronic spins, the Overhauser effect rather than the solid state effect is observed even for fixed paramagnetic impurities in InP. Due to the frequent spin flips between neighboring paramagnetic centres, there is a rapid motion of the orientation of the electron spin (as compared to the motion of electron itself).

3.5 Spin Diffusion

The concept of nuclear spin diffusion was first introduced by Bloembergen\(^ {52}\). He showed that spin diffusion plays an important role in nuclear magnetic relaxation in diamagnetic crystals with small concentrations of paramagnetic atoms. It was shown later that spin diffusion also plays an important role in induced dynamic polarization of nuclei in such a system. Due to the recent interest in dynamic nuclear polarization schemes, investigation of spin diffusion of nuclear spins has also received much attention lately. In this section, the basic theory of
nuclear spin diffusion and its importance in dynamic nuclear polarization in semiconductors is outlined.

Consider, for simplicity, a linear chain of spin \( \frac{1}{2} \) nuclei separated by a fixed interval \( (a) \) where a mutual flip of nearest neighbour spins occurs via dipolar interaction. It can be shown that the spin polarization obeys a diffusion equation of the type:

\[
\frac{\partial M(x,t)}{\partial t} = Wa^2 \frac{\partial^2 M}{\partial x^2} \quad (3.12)
\]

Where \( M(x,t) \) is the z-component of the magnetization at position \( x \) and time \( t \) and \( W \) is the probability per unit time for a mutual spin flip. Eqn. 3.12 can be extended to a three dimensional case giving,

\[
\frac{\partial M(r,t)}{\partial t} = D \Delta M
\]

where \( M(r,t) \) is the z-component of the magnetization at position \( r \) and time \( t \) and \( D \) is the coefficient of diffusion of the nuclear spin. \( D \) is a symmetrical tensor of second rank whose components depend on the angle between the external field and the crystal axes. In case of a cubic single crystal, polycrystalline sample or powder, \( D \) reduces to a scalar. Confining ourselves to the case of a cubic crystal and assuming only flip-flop transitions between nearest neighbours, we have:

\[ D \approx Wa^2 \]

For a cubic crystal, by averaging over directions an estimate\(^53\) of \( W \) can be obtained as:

\[ W \approx \frac{1}{30T_2} \]

where \( T_2 \) is the transverse time of nuclear relaxation.

Usually in a solid, \( T_2 \approx 10^{-5} \text{ sec} \), \( a \approx 5\times10^{-8} \text{ cm} \). This yields \( D \approx 10^{-11} \text{ cm}^2/\text{sec} \).

In the picture described above, we have assumed that \( W \), and hence \( D \), is constant throughout the sample. In reality, however, \( D \) is a function of distance from the nearest electron spin. This dependency comes from the fact that the Zeeman frequencies of the nuclei located near the electron spins differ appreciably from one another (owing to the magnetic field produced by the electron). This hinders the flip-flop transitions of the neighbouring nuclei since for such a transition the total Zeeman energy is no longer conserved. In a simplified model, one can assume that around each electron spin (paramagnetic centre), there exists a diffusion barrier, inside of which the diffusion of the nuclear spin is strongly hindered. An estimate of diffusion barrier radius can be obtained by introducing the distance from the paramagnetic centre, for which the difference of the Zeeman frequencies of the neighbouring nuclei is of the order of the width of the magnetic resonance. This distance is of the
order of \((\gamma_e/\gamma_n)^{1/4}a\). Thus, it is a reasonable approximation to assume that nuclei within this radius do not participate in spin diffusion. A schematic representation of spin diffusion model is shown in Fig. 3.6.

![Diffusion barrier](image)

**Fig. 3.6: A schematic representation of nuclear spin diffusion model.**

### 3.5.1 Spin Diffusion in Semiconductors

As mentioned in the previous section, spin diffusion dominates in systems with low concentration of paramagnetic impurities. Various theoretical as well as experimental studies have led to our present understanding of nuclear relaxation via paramagnetic impurities. It is well understood that the nuclei close to these centres relax directly by the electrons trapped on them whereas the bulk nuclei relax through transport of magnetization by spin diffusion from the centres. However, the fact that the number of nuclei close to impurities is much less than the bulk nuclei makes the study of two types of relaxation mechanisms difficult in NMR experiments.

n-type semiconductors with low doping concentrations are an excellent system where the resonance of nuclei close to the shallow donors can be observed selectively by means of optical pumping. Optical excitation in direct gap semiconductors is known to create effective electron spin polarization depending upon the electron recombination time and electron spin lifetime of the photoexcited electrons. These polarized electrons may become localized at impurity centres or defects. Such electronic states act as shallow donor levels and are commonly termed as "optically relevant defects." They have 1s-type hydrogenic states given by the effective mass theory. Nuclei in the vicinity of these defects get
dynamically polarized under the effect of strong hyperfine interaction. In the literature, the most commonly used model for explaining the polarization of bulk nuclei in OPNMR is the nuclear spin diffusion mediated by dipolar interactions between like neighbouring spins\textsuperscript{31} Fig. 3.7(a) shows OPNMR resonances of \textsuperscript{69}Ga in Semi-insulating GaAs as a function of laser illumination time ($\tau_L$) for two different helicities of light measured by K. Ramaswamy et al\textsuperscript{56}. The resonances show an optically induced hyperfine shift to higher frequencies and lower frequencies for $\sigma^+$ and $\sigma^-$ light respectively with respect to the reference signal from "bulk" GaAs at 6K. Simulated on to the data points in fig. 3.7(b) are the curves for the predicted evolution of shift based on the model of nuclear spin diffusion (using D=2300Å$^2$/s). The measured decay of hyperfine shift with irradiation time lends support to the mechanism of polarization by nuclear spin diffusion. Earlier OPNMR investigations on semiconductors have shown similar results\textsuperscript{57,54}

**Fig.3.7 (a) \textsuperscript{69}Ga OPNMR spectra. Helicity of the light, illumination time and the number of transients recorded are indicated on the figure. The black vertical line is a guide at the position of the reference spectrum. Figure taken from reference[56]**
Chapter 3: Magnetic Resonance

3.6 Overhauser Shift Spectroscopy

An investigation of the distribution of conduction electrons in semiconductors can be performed by measurement of the Knight shift or the Overhauser shift. Knight shift, which is the frequency shift of the NMR resonance due to coupling to electrons, is proportional to the probability $|\psi(r)|^2$ of the electron wavefunction at the nuclear position $r$ and to the conduction electron density. In case of semiconductors with low electron density, the Knight shift is small and hence its precise measurement is difficult. The Overhauser shift, on the other hand, is proportional to the probability $|\psi(r)|^2$ of the electron wavefunction at the nuclear position $r$ but is independent of conduction electron density. Overhauser Shift spectroscopy is thus a useful tool for investigation of hyperfine interaction in semiconductors. Theoretical and experimental aspects of this technique are described in this section.
The spin Hamiltonian for a system where a nuclear spin ($I=1/2$) is coupled to an electron spin $S=1/2$, acted on by an external magnetic field $B_0$ is given by:

$$\hat{H} = g^* \mu_b B_0 S_z + A S - \gamma_n \hbar B_0 I_z$$  \hspace{2cm} (3.13)$$

where $B_0$ is the static field along $z$, $\mu_b$ the Bohr magneton, $\gamma_n$ the nuclear gyromagnetic ration and $g^*$ the effective g factor of the electron. Considering only the spin Hamiltonian for the electron spin $S=1/2$,

$$\hat{H} = g^* \mu_b B_0 S_z + A S$$

For conduction electrons in metals and semiconductors, the correlation time $\tau_c$ of the electron at a nuclear position is of the order of $10^{-15}$ s and $\frac{1}{\tau_c} \gg \frac{A}{\hbar}$.

As a result, only an averaged hyperfine interaction is observed and the effective ESR Hamiltonian may be written as

$$\hat{H} = g^* \mu_b B_0 S_z + \langle A I \rangle_z S_z$$

Where $\langle A I \rangle_z$ is the ensemble average over all the nuclei of the lattice of a similar type. We may replace $\langle A I \rangle_z / (g^* \mu_b)$ by $B_n$, which is the nuclear field experienced by the electrons. In case of a homogeneous semiconductor, all nuclei of one type have equivalent hyperfine constant ($A$) and if the isotope has 100% natural abundance, the nuclear field simplifies to $B_n = A \langle I \rangle_z / (g^* \mu_b)$ and the ESR Hamiltonian simplifies to:

$$\hat{H} = g^* \mu_b (B_0 + B_n) S_z$$

The ESR resonance field is thus shifted by an amount $B_n$ which is known as the Overhauser shift.

The basic experiment for Overhauser shift measurement involves application of a saturating radio frequency field at the NMR frequency of the respective nucleus. The saturating field reduces the nuclear spin polarization and hence the nuclear field $B_n$ to zero. The ESR line thus shifts towards higher fields. The magnitude of the shift gives a direct measure of nuclear field $B_n$. Subsequently, nuclear spin lattice relaxation occurs and as the nuclear polarization builds up to its equilibrium value, the ESR line shifts back to its original position where it was before the saturation of nuclear polarization. The recovery of the ESR line position
thus occurs on the time scale equivalent to the nuclear spin lattice relaxation time.

### 3.7 Knight Shift/Paramagnetic Shift

Another consequence of strong hyperfine interaction is the shift of nuclear resonance frequency due to the influence from the surrounding electrons. This shift is known as the Knight shift (due to conduction electrons in metals) or paramagnetic shift (due to paramagnetic centres or localized donor electrons).

One can see from Hamiltonian (3.13) that the hyperfine interaction results in a shift of the nuclear resonance frequency given by:

\[ \Delta B = A \langle S \rangle_z / (h \gamma_n) \]

where \( A(r) \) is the contact hyperfine interaction given by:

\[ A(r) = \left( \frac{8\pi}{3} \right) \cdot \left( \frac{\mu_0}{4\pi} \right) \cdot g \mu_B h \gamma_n |\psi(r)|^2 \]

Thus, the relative shift of the nuclear frequency may be written as:

\[ K(r) = \frac{A(r)S_0(1 - s_{esr})}{\gamma_n h B_0} \times 10^6 \]

where \( K \) is the PM shift (in ppm), and \( s_{esr} \) is the ESR saturation factor defined by:

\[ s_{esr} = \frac{\langle S_z \rangle - \langle S_z \rangle}{\langle S_0 \rangle} \]

An important relation between nuclear spin relaxation time \( T_1 \) and Knight shift was introduced by Korringa and is known as the Korringa relation:

\[ T_1 \left( \frac{\Delta B}{B_0} \right)^2 = \frac{h}{4\pi kT} \left( \frac{\gamma_e}{\gamma_n} \right)^2 \]
Chapter 4

Resistivity and Relaxation Measurements

Dynamic nuclear polarization in semiconductors depends very strongly on the electron concentration in the conduction band as well as the concentration of localized electron centres. Furthermore, for dynamic nuclear polarization to exist, strong hyperfine coupling (and concomitant nuclear relaxation via electrons) is a crucial requirement. Thus, before commencing a study of DNP, a careful analysis of the hyperfine interaction in semiconductors is imperative. Especially, the dependence on electron concentration has to be clarified.

For this purpose, we studied InP and GaAs samples with varying doping concentrations. Table 2.1 shows a list of the samples along with their respective doping concentrations, type of doping and dopants. The temperature dependence of resistivity was studied in these samples in order to investigate the extent of localization of electrons. The temperature dependence of nuclear spin lattice relaxation was used to elucidate the dominant mechanism of nuclear relaxation for various nuclei in InP and GaAs.
4.1 Resistivity Measurements

Several studies have been conducted on optically induced DNP in III-V semiconductors\textsuperscript{58,59} in general and GaAs\textsuperscript{41,60,61} in particular and various models have been proposed to explain the observed DNP till date. While some models propose\textsuperscript{56} that the observed DNP cannot be due to free electrons, other models\textsuperscript{62} show that the source of enhanced nuclear polarization are neither completely localized nor completely delocalized electrons. In order to estimate the exact contribution of localized and itinerant electrons in creating DNP, the extent of electron localization should be known. For this purpose, a detailed investigation of resistivity and its temperature dependence was carried out on samples shown in table 4.1.

<table>
<thead>
<tr>
<th>Sample Number (Type)</th>
<th>III-V material</th>
<th>Dopant</th>
<th>Doping(cm\textsuperscript{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (metallic)</td>
<td>nGaAs</td>
<td>Si</td>
<td>$2.1 \times 10^{18}$</td>
</tr>
<tr>
<td>2 (just metallic)</td>
<td>nGaAs</td>
<td>Si</td>
<td>$2.5 \times 10^{16}$</td>
</tr>
<tr>
<td>3 (insulating)</td>
<td>nGaAs</td>
<td>Si</td>
<td>$1.2 \times 10^{15}$</td>
</tr>
<tr>
<td>4 (metallic)</td>
<td>nInP</td>
<td>S</td>
<td>$(0.8-8) \times 10^{18}$</td>
</tr>
<tr>
<td>5 (semi-insulating)</td>
<td>SI InP</td>
<td>Fe</td>
<td>-</td>
</tr>
<tr>
<td>6 (just insulating)</td>
<td>Undoped InP</td>
<td>S,Si (residual)</td>
<td>$7 \times 10^{15}$</td>
</tr>
</tbody>
</table>

Electrical contacts were made on semiconductor wafers by evaporating thin Au-Ge stripes (by using electron gun technique). The thickness of the stripes was limited to ~50nm in order not to block radiofrequency at the NMR frequency (58MHz). This enabled NMR measurements on these samples. A wafer of GaAs with Au-Ge contacts is shown in fig. 4.1

![Fig. 4.1: GaAs sample with electrical contacts in the form of Au-Ge stripes](image-url)
SI InP (sample#5) has a very high room temperature resistivity (>MOhm-cm) and hence temperature dependent measurement could not be performed on this sample. Metallic InP and GaAs samples (#4 and #1) on the other hand are highly doped and hence no localization of electrons is expected in these samples. Samples close to Metal Insulator Transition (MIT) (#2, #3 and #6) however, show interesting behaviour with respect to temperature dependence.

Fig. 4.2(a) shows the resistivity vs. inverse temperature measurement for just metallic GaAs (#2). It is seen that the resistivity is only slightly dependent on temperature below 20K. The resistivity data below 20K can be fit with $\sigma = \exp(-\sqrt{\frac{T_1}{T}})$ (Fig. 4.2(b)), consistent with variable range hopping conduction. Above 20K, the resistivity decreases with increasing temperature due to changes in mobility. The insulating GaAs sample (#3) on the other hand has much lower doping concentration and thus very high resistivity. Resistivity below 80K is greater than MΩ and beyond our measurement range. Below 190K, $\sigma = \exp(-\sqrt{\frac{T_1}{T}})$ dependence is observed (Fig. 4.3(b)).

![Resistivity vs. Temperature for just-metallic-GaAs](image)

*Fig. 4.2(a): Resistivity vs. Temperature for just-metallic-GaAs (sample#2, doping $= 2.5 \times 10^{16} \text{ cm}^{-3}$)*
Chapter 4: Resistivity and Relaxation Measurements

Fig. 4.2(b): ln(\(\sigma\)) vs. \(T^{-1/2}\) for metallic-GaAs (sample #2, doping = \(2.5 \times 10^{16} \text{ cm}^{-3}\))

Fig. 4.3(a): Conductivity vs. Temperature for insulating-GaAs (sample #3, doping = \(1.2 \times 10^{15} \text{ cm}^{-3}\))
Chapter 4: Resistivity and Relaxation Measurements

Fig. 4.3(b): $\ln(\sigma)$ vs. $T^{-1/2}$ for insulating-GaAs (sample #3, doping = $1.2 \times 10^{15}$ cm$^{-3}$)

Fig. 4.4: $\ln(\sigma)$ vs. $T^{-1/2}$ for undoped InP (sample #6, doping=$7 \times 10^{15}$ cm$^{-3}$)
Chapter 4: Resistivity and Relaxation Measurements

Ln(conductivity) vs. T^{-1/2} for undoped InP (sample #6) is shown in fig. 4.4. Above about 50K, the resistivity changes exponentially with 1/T due to thermal activation of localized donors. Below 30K, variable range hopping conduction ($\sigma = \exp(-\sqrt{T/T_i})$) is observed.

One may draw two conclusions from the resistivity analysis described above:

Firstly, for n-type GaAs and InP wafers with doping concentration close to MIT, transport in low electric fields occurs mainly through variable – range hopping at low temperatures. However, at high electric fields and low temperatures, impact ionization is known$^{65,66}$ to excite carriers into the conduction band. Thus, one may conclude that in just-metallic GaAs (#2) and undoped InP (#6) low temperature conduction involves hopping between localized states as well as conduction band transport. The dominant conduction mechanism depends on the applied electric field. Electron hopping results in motionally narrowed ESR lines and strongly affects DNP processes in these semiconductors. We shall discuss these effects in detail in the following chapters.

Secondly, insulating GaAs (sample #3) is not a suitable sample for study of current induced dynamic nuclear polarization due to its high resistivity, especially at low temperatures. This is in contrast to optical DNP experiments where semi-insulating semiconductors are preferred in most studies.

4.2 NMR spectra

NMR was measured for all magnetic isotopes of samples listed in table 4.1. Measurements were performed in an 8T Oxford magnet (with homogeneity of 10 ppm/10mm diameter spherical volume) with a homemade pulsed NMR spectrometer. Standard GaAs and InP wafers were cleaved to give samples of dimensions 4\times2\times0.3mm$^3$. The sample surface was aligned orthogonal to the external magnetic field. Various measured nuclei, the magnetic field at resonance and other properties of these nuclei are listed in table 4.2. All the measured nuclei gave a single NMR line of linewidth in the range 30-60 ppm. This linewidth is mainly due to dipolar broadening since both GaAs and InP have cubic symmetry and hence no quadrupolar splitting is expected. Fig.4.5 shows a typical $^{75}$As NMR signal (after Fourier transform) at 300K from n-type GaAs sample of dimensions 8\times4\times0.5 mm$^3$. The signal can be fitted by a Gaussian function and has 1.8kHz (~30ppm) linewidth.
Chapter 4: Resistivity and Relaxation Measurements

4.3 Nuclear Spin Lattice Relaxation

Dynamic nuclear polarization (DNP) results from transfer of spin polarization from electrons to nuclei. The two most important prerequisites for this process are:

- The electron spin system must be driven out of thermal equilibrium
- The nuclear system must be coupled to the electron system

In III-V semiconductors, hyperfine interaction is the dominating coupling mechanism between electrons and nuclei. The importance of HFI in DNP
experiments has been highlighted in a number of recent experiments \(^{67,41,31,68,69,70}\). Relaxation rate measurements on samples with different doping concentrations and in a wide temperature range provide useful information about various nuclear relaxation mechanisms operating at different temperature ranges. Temperature ranges favourable for relaxation via hyperfine coupling to electrons can thus be determined by means of nuclear relaxation measurements.

We measured nuclear spin lattice relaxation rates for various nuclei in the temperature range 8K-300K for all the samples listed in table 4.1. Temperatures in the above mentioned range were obtained using a continuous flow cryostat (Oxford Instruments, CF1200) and temperature controller (Oxford Instruments, ITC4). The nuclear spin lattice relaxation time (\(T_1\)) was measured using saturation recovery method (saturating the nuclear magnetization using a comb of 90° pulses and measuring the recovery of FID signal). In samples with low doping concentration, \(T_1\) is very long especially at low temperatures. In these samples \(T_1\) measurements were performed by means of a method similar to Fast Low Angle Shots imaging (FLASH) in order to avoid long waiting periods between two successive measurements. The pulse sequence used for such measurements is shown in fig. 4.6(a). Nuclear spin lattice relaxation time measurement for \(^{75}\text{As}\) in GaAs is shown in fig. 4.6(b). The temperature dependence of \(T_1\) for various nuclei measured in GaAs and InP is shown in fig. 4.7 to 4.13.

![Fig. 4.6(a): Pulse sequence used for nuclear spin lattice relaxation rate measurement at low temperature. The recovery of the longitudinal magnetization (\(M_z\)) after saturation is shown in dotted line.](image-url)
Fig. 4.6(b): $^{75}\text{As } T_1$ measurement at 8K in GaAs (doping = $2.5 \times 10^{16}$ cm$^{-3}$). Fitting of data with a function: $M_z(t) = M_0(1 - e^{-t/T_1})$ gives $T_1 \sim 10$ min.

Fig. 4.7 shows Log-Log plot of $^{75}\text{As}$ nuclear spin lattice relaxation time ($T_1$) as function of temperature for GaAs samples with different doping concentrations (sample#1 and sample#2). Lines are linear fits to the measured data points. At high temperatures, the measured $T_1$ for the two samples converge which is consistent with the measurements of Neil and Clark$^{71}$. At $T > 20$K, the relaxation time increases approximately with $1/T^2$ dependence. This is a signature of two phonon quadrupolar relaxation$^{71}$. In the temperature range 8K-20K, the measured $T_1$ increases linearly with temperature. This is a characteristic of Korringa type relaxation in metals and is applicable to semiconductors in metallic regime. $^{69}\text{Ga } T_1$ measurements (fig. 4.8) show a similar behaviour.
Chapter 4: Resistivity and Relaxation Measurements

Fig. 4.7: log-log plot of $^{75}$As nuclear spin lattice relaxation time ($T_1$) as function of temperature for GaAs samples with different doping concentrations (in cm$^{-3}$). Lines are fits to the measured data points.

Fig. 4.8: log-log plot of $^{69}$Ga nuclear spin lattice relaxation time ($T_1$) as function of temperature for GaAs samples with different doping concentrations (in cm$^{-3}$). Lines are fits to the measured data points.
A comparison of fig. 4.7 and fig. 4.8 shows that the temperature at which the relaxation mechanism changes from quadrupolar to Korringa type is about 15K for $^{75}$As and 25K for $^{69}$Ga. Quadrupolar moments of $^{75}$As and $^{69}$Ga nuclei are listed in table 2.1. It is seen that the quadrupolar moment of $^{75}$As is almost twice that of $^{69}$Ga. Quadrupolar relaxation is thus more pronounced in $^{75}$As nuclei as compared to $^{69}$Ga nuclei. Furthermore, the dopants (Si in this case) substitute Ga nuclei in GaAs lattice. This substitution causes distortions in the lattice close to the Si position. The distortion is maximum at the position of the nearest neighbours (As in this case) leading to higher electric field gradient and higher probability of relaxation via phonons.

The metal-insulator transition in GaAs$^{72,73}$ occurs at $n = 1.2 \times 10^{16}$ cm$^{-3}$. Thus, sample #1 ($n = 2.1 \times 10^{18}$ cm$^{-3}$) is completely metallic whereas sample #2 ($n = 2.5 \times 10^{16}$ cm$^{-3}$) is just metallic. For metallic samples, spin relaxation is due to scattering processes involving conduction electrons close to the Fermi level. In such a scenario, the relaxation rate via contact hyperfine interaction is given by$^{74}$:

$$\frac{1}{T_1} = \frac{64\pi^3}{9} \gamma_e \gamma_n \hbar^3 \left\langle \phi_F(0) \right\rangle^4 \rho(E_F)^2 kT$$

with $\gamma_e$ and $\gamma_n$ the gyromagnetic ratios for the free electron and the nucleus respectively, $\hbar$ Planck’s constant, $\rho(E_F)$ the density of states at the Fermi level and $k_B$ Boltzmann constant. In the free electron gas model, $\rho(E_F)$ is proportional to $n^{1/3}$, where $n$ is the electron concentration. Thus, the relaxation rate ($W$) is proportional to $n^{2/3}$. As a result, the relaxation rate for sample #1 should be about 10 times faster than that of sample #2. Fig. 4.9 and 4.10 show $T_1$ for $^{69}$Ga and $^{75}$As nuclei for sample #1 and #2 in temperature range 8K-15K. It is seen that the ratio of relaxation rates is $\sim 3$ (and not 10). This suggests that nuclear spin lattice relaxation in just metallic sample (#2) in temperature range 8K-15K is not by conduction electrons but by means of interaction between localized electrons and its neighbouring nuclear spins in combination with spin diffusion to the bulk nuclei.
Fig. 4.9: Plot of $^{69}$Ga nuclear spin lattice relaxation time ($T_1$) as function of temperature for GaAs samples with different doping concentration.

Fig. 4.10: Plot of $^{75}$As nuclear spin lattice relaxation time ($T_1$) as function of temperature for GaAs samples with different doping concentration. Lines are fits to the measured data points.
A comparison of temperature dependence of nuclear spin lattice relaxation time for just metallic sample#2 \((n = 2.5 \times 10^{16} \text{ cm}^{-3})\) and insulating sample#3 \((n = 1.2 \times 10^{15} \text{ cm}^{-3})\) is shown in fig.4.11. It is observed that at \(T>30\text{K}\), the relaxation times for the two samples are similar. Since the doping concentrations of these samples differ by a factor of 21, the observed similarity in \(T_1\) times further confirms the fact that at \(T>30\text{K}\), electrons are not involved in the nuclear relaxation processes. At temperatures lower than 30K, however, the role of electrons becomes dominant (Korringa type behaviour at \(T<30\text{K}\) for just metallic sample). Owing to the huge difference in doping concentrations, the measured \(T_1\) times for the two samples show difference at lower temperatures. For example at 10K, \(T_1\) of insulating sample is 26 times longer than the \(T_1\) in just metallic sample. It is to be noted that this observation is not in accordance with similar measurements done by Lu et al\(^{46}\). The authors find only subtle differences between \(T_1\) of GaAs samples with doping concentration \(n = 5.9 \times 10^{15} \text{ cm}^{-3}\) and \(n = 7 \times 10^{16} \text{ cm}^{-3}\). The observed discrepancy is due to difference in average distance between impurities in the insulating samples used by the authors and in our measurements. Relaxation on the insulating side of the MIT at low temperature is attributed to the interaction between localized electrons and nuclear spins in combination with spin diffusion. Lu et al\(^{46}\) demonstrate that the Fermi contact hyperfine interaction is 1000 times stronger than the dipolar hyperfine interaction when the distance between impurities is less than 500Å. For \(n = 5.9 \times 10^{15} \text{ cm}^{-3}\), average distance between impurities is \(~500\text{Å}\) and hence Fermi contact hyperfine interaction dominates. For \(n = 1.2 \times 10^{15} \text{ cm}^{-3}\), the impurities are separated by an average distance of \(~900\text{Å}\). Hence, dipolar contact interaction dominates, resulting in longer relaxation time in our insulating samples.

A plot of \(^{115}\text{In}\) and \(^{31}\text{P}\) nuclear spin lattice relaxation time (\(T_1\)) as function of temperature for n-InP (sample #4) is shown in fig.4.12. Lines are fits to the measured data points.\(^{115}\text{In}\) measurements show signs of quadrupolar relaxation for \(T>50\text{K}\). At lower temperatures, \(T_1\) increases linearly with decrease in \(T\). One may conclude that \(^{115}\text{In}\) undergoes quadrupolar relaxation for \(T>50\text{K}\) and Korringa type relaxation for \(T<50\text{K}\). \(^{31}\text{P}\) nuclei however show Korringa relaxation in the entire temperature range. This is expected since \(^{31}\text{P}\) is a spin \(\frac{1}{2}\) nucleus and hence cannot undergo quadrupolar relaxation.
Chapter 4: Resistivity and Relaxation Measurements

Fig. 4.11: Log-log plot of $^{75}$As nuclear spin lattice relaxation time ($T_1$) as function of temperature for just metallic and insulating GaAs.

Fig. 4.12: Log-Log plot of $^{115}$In and $^{31}$P nuclear relaxation time ($T_1$) as function of temperature for n-InP (sample #4). Lines are fits to the measured data points.
\[ \frac{1}{T_1} = \frac{64\pi}{9} n \gamma_e^2 \gamma_n^2 \hbar^3 |\varphi_e(0)|^4 \left( \frac{m^* kT}{2\pi} \right)^{1/2} \] (4.2)

where \(|\varphi_e(0)|^2\) is the electronic density at the nucleus for an electron of energy \(E\) and \(n\) is the total number of conduction electrons per unit volume. The most remarkable feature of eqn. 4.2 is the proportionality of \(1/T_1\) to \(T^{1/2}\), which is to be contrasted with the \(T\) dependence in case of metals and semiconductors above MIT. The undoped InP (sample #6) used in our measurements has doping concentration less than the MIT concentration (\(\approx 10^{16} \text{cm}^{-3}\)). Thus, the observed \(T^{-0.4}\) dependence is consistent with relation 4.2 as expected. Similar \(T^{-0.4}\) dependence has been observed for the case of insulating GaAs earlier\(^{46}\).

The temperature dependence of \(T_1\) for \(^{115}\text{In}\) in SI- InP (sample #5) is shown in fig. 4.14. \(^{115}\text{In}\) \(T_1\) shows \(\sim T^{-2}\) dependence as expected for quadrupolar relaxation (since in SI samples, electron concentration is very low). \(^{31}\text{P}\) has very long \(T_1\) in this sample and hence the temperature dependence could not be measured.
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Fig. 4.13: log-log plot of $^{115}\text{In}$ and $^{31}\text{P}$ nuclear spin lattice relaxation time ($T_1$) as function of temperature for undoped InP (sample #6). Lines are fits to the measured data points.

Fig. 4.14: log-log plot of $^{115}\text{In}$ nuclear spin lattice relaxation time ($T_1$) as function of temperature for SI-InP (sample #5). Lines are fits to the measured data points.
4.5 Conclusion and Outlook

As was pointed out in section 3.4, semiconductors with partially delocalized electrons (with motionally narrowed ESR lines) exhibit Overhauser type dynamic nuclear polarization. We have seen in our resistivity measurements that just-metallic GaAs (#2) and undoped InP (#6) show hopping-type of conduction at low temperatures (<20K). Insulating GaAs (sample #3) and InP (sample #5) show carrier freeze out effects and hence cannot be used to study current-induced dynamic nuclear polarization at low temperatures. Nuclear spin lattice relaxation measurements have shown that quadrupolar relaxation is predominant at high temperatures whereas relaxation via hyperfine coupling to electrons sets in at low temperatures (<20K) in all the samples studied. Since, DNP requires strong electron-nuclear coupling, cooling to temperatures lower than 20K is imperative for DNP to build up.

In conclusion, low doped GaAs and InP semiconductors at low temperatures (<20K) appear to be favourable systems where dynamic nuclear polarization processes are likely to be operating. Before attempting to study current induced DNP, we perform Overhauser shift experiments in these samples in order to estimate DNP parameters. These are described in the next chapter.
Chapter 5

InP: ESR and Overhauser Spectroscopy

The investigated InP crystals were Liquid Encapsulated Czochralski (LEC) grown undoped crystals (sample#5) commercially available from Wafer Technology. The crystals were unintentionally doped in the carrier concentration range $6.7 \times 10^{15} - 8 \times 10^{15} \text{cm}^{-3}$. Silicon and sulphur are common residual impurities known to exist in InP$^{76,77}$. The ESR experiments were performed on a commercial X-Band (10GHz) ESR spectrometer (from Bruker) along with continuous flow liquid helium cryostat. All experiments reported were carried out at 8K.

5.1 The ESR Spectra

Localized defects in III-V semiconductors are known to exhibit ESR spectra with broad Gaussian lines. Unresolved ligand hyperfine interactions of the unpaired electrons with spins of the host lattice nuclei are believed to be responsible for such broad lines. The ESR signals observed in our measurements from this sample have almost Lorentzian lineshape and linewidth $\sim 1.8$ Gauss. A typical ESR line at 8K and 0.2mW microwave power is shown in fig.5.1. The narrow Lorentzian lineshape is expected for completely or partially delocalized electrons moving in overlapping shallow donor orbits and impurity bands. Motional
narrowing due to hopping processes of these electrons leads to narrow, nearly Lorentzian lineshapes as seen in our measurements.

![Graph showing ESR spectrum with data and fitting curves.](image)

\[ \text{Amplitude (Arb. units)} \]

\[ B(G) \]

**Fig. 5.1: InP ESR spectrum at 8K. } f_{\mu}\text{=9.4173GHz, } g=1.204 . \text{ The fitting function is a derivative of Lorentian at } B= 5589G \text{ and linewidth } = 1.79G.\]

### 5.2 The Overhauser Shift

As explained in section 2.3, by strong ESR saturation, the nuclear polarization is enhanced through hyperfine interaction between electrons (conduction or donor) and nuclear spins, leading to a shift of the ESR line to lower external field. This shift is known as the Overhauser shift.

In order to measure the Overhauser shift in InP, partial ESR saturation was carried out by means of a slow downward magnetic field sweep at high microwave power. Since the Overhauser shift causes the ESR line to shift to lower fields, during a slow downward sweep of the external magnetic field, the resonance field for ESR also decreases and the resonant condition continues to be fulfilled during magnetic field sweep. In this case the nuclear spin polarization is increased steadily and hence a large Overhauser shift is seen. The measured Overhauser shift showed a strong dependence on the speed of downward field sweep. Maximum shift was observed for a sweep speed 30G/min and hence this speed was
used for all the measurements. After the ESR saturation, the ESR spectrum was recorded at fixed time intervals by means of fast sweeps at very low microwave powers. This enabled us to follow the recovery of the nuclear polarization to the thermal equilibrium value.

Fig.5.2 shows the ESR line position recorded at fixed time intervals after ESR saturation. By saturating the ESR at 11dB (16mW) microwave power, we dynamically polarize the nuclei, hence shifting the line to 5545Gauss. After the saturation, subsequent fast ESR scans are carried out at a very low microwave power (0.08mW). This is shown in line positions (a) – (f). The difference in the line positions (a) and (f) gives the Overhauser shift at 11 dB microwave power. Moreover, since the recovery of nuclear polarization occurs with a time constant $T_1$ (nuclear spin lattice relaxation) at that temperature, the ESR line shifts back to its thermal equilibrium position on the same time scale. The $T_1$ of nuclei responsible for the Overhauser shift can thus be determined from the plot of ESR line position vs. time. This is shown in fig.5.3.

![Fig.5.2: InP ESR spectra recorded at fixed time intervals after inducing DNP by partial saturation of ESR line at 16mW microwave power at 8K.](image_url)
Fig. 5.3: Overhauser shift as a function of time after ESR saturation at 16mW microwave power. The fitting with a mono-exponential decay function gives $T_1 = 100$ s.

It is seen from fig. 5.2 that the ESR saturation not only leads to ESR line shift but also results in inhomogenous broadening of the ESR lines. This is an indication of the fact that the observed ESR does not originate from conduction electrons but from bound donor electrons. As explained in section 3.1, shallow donors in semiconductors have extended wavefunctions. In InP the wavefunction of a donor is extended to $\sim 85\text{Å}$. The nuclei within this radius experience strong HFI which varies with the distance from the donor. As a result, the induced DNP (and the resultant Overhauser shift) depends on the distance of the nuclei from the donor. This leads to an inhomogenous broadening of the ESR line upon saturation. Moreover, usually there exists more than one type of residual impurities which act as donors in an undoped semiconductor. Additionally, since the distribution of donors is inhomogenous within a semiconductor, the ESR line is also inhomogenous. The shallow donors in a III-V semiconductor have a tendency to form clusters\textsuperscript{78}. The presence of clustering in our samples was confirmed by an observed splitting of the ESR line at very high microwave power. Upon ESR saturation, each donor cluster shifts its own resonance to lower magnetic fields due to Overhauser shift leading to splitting and broadening of ESR line as shown in shown in fig. 5.4.
Fig. 5.4: ESR spectra recorded at fixed time intervals after inducing DNP by partial saturation of ESR line at 50mW microwave power and 8K.
The total Overhauser shift in InP has contribution from various nuclei ($^{115}$In, $^{113}$In, and $^{31}$P). The properties of these nuclei are mentioned in table 5.1.

**Table 5.1. Nuclei in InP**

<table>
<thead>
<tr>
<th>Nuclei</th>
<th>I</th>
<th>Abundance</th>
<th>$\gamma$ (s⁻¹T⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{115}$In</td>
<td>9/2</td>
<td>95.7%</td>
<td>$5.862 \times 10^7$</td>
</tr>
<tr>
<td>$^{113}$In</td>
<td>9/2</td>
<td>4.3%</td>
<td>$5.849 \times 10^7$</td>
</tr>
<tr>
<td>$^{31}$P</td>
<td>1/2</td>
<td>100%</td>
<td>$10.83 \times 10^7$</td>
</tr>
</tbody>
</table>

In thermal equilibrium, the nuclear polarization $\langle I_z \rangle$ for the three nuclei follows Brillouin-Curie law and we have,

$$\langle I_z \rangle \approx \frac{\hbar \gamma \mu I(I+1)B}{3kT}$$  \hspace{1cm} (5.1)

where $B$ is in Tesla and $T$ in Kelvin. From eqn.5.1 one can see that the thermal equilibrium value $\langle I_z \rangle$ for $^{115}$In exceeds that of $^{31}$P by a factor of almost 18. Thus, the contribution from $^{31}$P to the total Overhauser shift can be ignored. Also, due to low natural abundance of $^{113}$In, we may assume that the Overhauser shift measured in InP by the above mentioned method comes mainly from $^{115}$In nuclei.

In order to measure the shifts due to $^{31}$P nuclei, the double resonance technique was used as described in the following section.

### 5.3 Overhauser Shift Measurement by Double Resonance

Since the Overhauser shift due to $^{31}$P nuclei is very small compared to the contribution from $^{115}$In nuclei, the method described above cannot be used for measurement of the $^{31}$P contribution to the total Overhauser shift. Also, in order to measure the Overhauser shift due to $^{115}$In nuclei at thermal equilibrium, the nuclear spin polarization must be reduced to zero. This is achieved by double resonance experiments as described below.

The basic double resonance experiment for measurement of the Overhauser shift involves reducing the nuclear spin polarization to zero by application of a saturating radiofrequency field at the NMR frequency of the respective nucleus. These measurements were performed in a dielectric cavity and a special sample holder for RF application. One may use an ENDOR cavity for this purpose but a dielectric cavity has a much...
larger Q factor. A sample holder with one loop around the sample acting as a coil was constructed. The loop was made from printed circuit board (PCB) which gives an additional advantage of a perfect geometry and minimum metal inside the cavity. The sample holder is shown in fig 5.5(a). The NMR frequency was swept over an appropriate range by means of Rhode and Schwarz RF synthesizer controlled by an external HPVEE program.

That the RF loop shown in fig. 5.5(a) does indeed provide sufficient RF power to affect the nuclei can be seen from fig. 5.5(b) where the shift of the ESR line position with and without application of RF power on the loop is shown. When no RF (at the $^{115}$In nuclear resonance frequency) is applied, the ESR line position shifts to lower field by about 1.4G at 2.5mW of microwave power. However, with application of 0.02mW of RF power, the ESR line position stays constant within the experimental errors.

*Fig. 5.5(a): Sample holder with a single loop for RF application*
For double resonance measurements, the magnetic field is set to the value corresponding to the electron spin resonance condition. The radiofrequency field is then swept over an appropriate range while ESR line position is measured. When the resonance frequency of nuclei being studied is reached, the nuclear polarization is reduced to zero and so is the Overhauser shift caused by these nuclei. As a result, the ESR line shifts to a higher magnetic fields and this is seen as a step. After passage through the NMR frequency, the nuclear polarization relaxes back to its equilibrium value with a time scale $T_1$ (nuclear spin lattice relaxation time). This leads to the recovery of the ESR line to its equilibrium position at the same time scale.

Fig 5.6 shows a typical Overhauser shift vs. radiofrequency curve for $^{115}$In nuclei. Above the resonance frequency, the shift signal relaxes exponentially with a time constant $= 105 s$. Similar measurements were performed for $^{31}$P nuclei. However since the contribution of $^{115}$In nuclei is much stronger than that of $^{31}$P nuclei, the $^{115}$In nuclei had to be kept depolarized in order to measure $^{31}$P shift accurately. This was done by sweeping the radiofrequency field across the $^{115}$In resonance frequency by means of a second RF synthesizer. Fig 5.7 shows Overhauser shift vs. radiofrequency curve for $^{31}$P. The nuclear $T_1$ is obtained by fitting of this curve with an exponential decay function which gives $T_1=175 s$. 

Fig.5.5 (b): Overhauser Shift of ESR line as function of microwave power with and without application of radio frequency on the RF loop.
Fig. 5.6: Overhauser shift vs. radiofrequency for $^{115}\text{In}$ at 8K. The fitting to the data after $f_{\text{res}}$ gives $T_1=105\text{s}$. Sweep time = 800s, $P_{\text{RF}}=0.25\text{mW}$, $P_{\mu\omega}=34\text{dB}$ (0.08mW)

Fig. 5.7: Overhauser shift vs. radiofrequency for $^{31}\text{P}$ at 8K. The fitting to the data after $f_{\text{res}}$ gives $T_1=175\text{s}$. Sweep time = 1200s, $P_{\text{RF}}=80\text{mW}$, $P_{\mu\omega}=34\text{dB}$ (0.08mW)
ESR Saturation Dependence

For a scalar hyperfine interaction, the dependence of the nuclear spin polarization \( \langle I_z \rangle \) on the ESR saturation is given by

\[
\langle I_z \rangle = \langle I_0 \rangle (1 + V s_{esr})
\]

(5.2)

where \( \langle I_0 \rangle \) is the nuclear spin polarization in thermal equilibrium and \( s_{esr} \) is the saturation parameter defined by

\[
s_{esr} = \frac{\langle S_0 \rangle - \langle S_z \rangle}{\langle S_0 \rangle} = \frac{(\gamma_e B_s)^2 \tau_1 \tau_2}{1 + (\gamma_e B_s)^2 \tau_1 \tau_2}
\]

(5.3)

with \( 0 < s_{esr} < 1 \).

\( V \) is the Overhauser enhancement factor which depends on the gyromagnetic ratios of the electron and the nucleus and a “leakage” factor \( f \):

\[
V = \frac{g_e^* \mu_B}{\hbar \gamma_n} \cdot f
\]

(5.4)

Using eqn 5.2 and 5.3, the dependence of Overhauser shift on microwave power can be described by:

\[
B_n = B_{n0} \left[ 1 + \frac{V \alpha P_{\mu W}}{(1 + \alpha P_{\mu W})} \right]
\]

(5.5)

where \( B_n \) is the Overhauser shift, \( B_{n0} \) is the thermal equilibrium value of the Overhauser shift. The Overhauser shift and \( T_1 \) was measured at different microwave powers for \(^{115}\)In at 8K using the technique described in section 3.2. It is to be noted that using this technique the measured shift is \((B_n - B_{n0})\) and not \( B_n \). Fig. 5.8 shows the measured Overhauser shift vs. microwave power for \(^{115}\)In nuclei. The data points are fitted with an expression of the form:

\[
B_n - B_{n0} = B_{n0} \left[ \frac{V \alpha P_{\mu W}}{(1 + \alpha P_{\mu W})} \right]
\]

(5.6)

From the fitting parameters the value of \( \alpha \) and the product \((B_{n0} \cdot V)\) are obtained for \(^{115}\)In nuclei as \( \alpha = 6.05 \times 10^{-3} \) mW\(^{-1}\) and \( B_{n0} \cdot V = 387 \) G respectively. Overhauser shift vs. \( s_{esr} \) is plotted in fig 5.9.
Fig. 5.8: (Overhauser shift - Overhauser shift at thermal equilibrium) as a function of microwave power for $^{115}$In nuclei at 8K. Fitting with a function $y = A\alpha/(1 + \alpha)$ where $\alpha = 6.05 \times 10^{-3}$ and $A=387$.

Fig. 5.9: (Overhauser shift-thermal equilibrium value) as a function of ESR saturation factor for $^{115}$In nuclei at 8K. The slope of the linear fit is 387.
In order to determine the value of \( B_{n0} \), Overhauser shift due to \(^{115}\text{In}\) nuclei coupled to the electrons was measured at low microwave powers. This was possible only by the double resonance technique. Fig 5.10 shows the dependence of \(^{115}\text{In}\) Overhauser shift on the microwave power in small power range. The extrapolation of this curve at \( P_{\mu w} = 0 \) gives the thermal equilibrium value of Overhauser shift caused by \(^{115}\text{In}\) nuclei as \( 1.508 \text{G} \) (269.7 ppm). Using this value and the product \( (B_{n0} \cdot V) \) obtained from fig.5.8, the DNP enhancement factor for \(^{115}\text{In}\) \( (V_{In}) \) is determined as 256.7.

![Graph](image)

**Fig. 5.10: Overhauser shift as a function of microwave power for \(^{115}\text{In}\) nuclei at 8K and \( B=5590\text{G} \). Extrapolation to \( P_{\mu w} = 0 \) gives \( B_{n0}=1.508\text{G} \) \( (D_0= B_{n0}/B=269.7\text{ppm}) \)**

Overhauser shift vs. \( P_{\mu w} \) for \(^{31}\text{P}\) is shown in fig 5.11. By extrapolating this plot to \( P_{\mu w} = 0 \) we obtain the thermal equilibrium shift value \( (B_{n0}) \) as 13.1 ppm. In order to determine the amplification factor \( (V_{P}) \) for \(^{31}\text{P}\), the Overhauser shift has to be measured as a function of microwave power over a reasonable range. This is not possible in InP sample due to strong influence from the In nuclei at high microwave powers. We may however assume the same ESR saturation parameter \( (s_{esr}) \) for \(^{31}\text{P}\) as in the case of \(^{115}\text{In}\) nuclei. This assumption is justified since all the factors on which the ESR saturation parameter depends (such as sample holder, temperature etc.) were kept constant during measurement on \(^{115}\text{In}\) and \(^{31}\text{P}\) nuclei. Using the value of \( \alpha \) from \(^{115}\text{In}\) measurements, we plot Overhauser shift vs. \( s_{esr} \) for \(^{31}\text{P}\) in fig. 5.12. From the slope of this curve, the amplification factor \( V_{P} \) is obtained for \(^{31}\text{P}\) as 454.8.
Fig. 5.11: Overhauser shift as a function of microwave power for $^{31}$P nuclei at 8K and $B=5590$G. Extrapolation to $P_{\mu w}= 0$ gives $B_{n0}=0.073$G ($D_0= B_{n0}/B=13.1$ppm)

Fig. 5.12: Overhauser shift as a function of ESR saturation factor for $^{31}$P nuclei at 8K. The slope of the linear fit= 454.8
RF Saturation Dependence

The Overhauser shift measured by the above mentioned method represents the true value of the nuclear field experienced by the electrons only when the nuclear polarization is completely reduced to zero. For incomplete depolarization of nuclei, the measured Overhauser shift is less than the complete nuclear field. In order to determine the degree of nuclear depolarization, a series of Overhauser shift measurements were performed at a fixed microwave power and varying radiofrequency power. The dependence of measured Overhauser shift on RF power follows a relation:

\[ B_n(P_{RF}) = B_n \cdot s_{RF} \]  

(5.7)

with

\[ s_{RF} = \frac{(\gamma_n B_2)^2 T_1 T_2}{1 + (\gamma_n B_2)^2 T_1 T_2} \]  

(5.8)

Thus, the RF saturation parameter for a nucleus depends on \( \gamma_n \), \( T_1 \), \( T_2 \) of the nucleus and the power of the RF field used.

The measured data is shown in fig 5.13 for \(^{115}\text{In}\). Fitting of the data points with a function of the form

\[ B_n(P_{RF}) = B_n \cdot \frac{\beta P_{RF}}{1 + \beta P_{RF}} \]  

(5.9)

gives the values of \( B_n \) and \( \beta \) as 4.47G and 2.18 mW\(^{-1}\) respectively. Using the value of \( \beta \), the RF saturation parameter \( s_{RF} \) is obtained. The inset of fig.5.13 shows the measured Overhauser Shift as a function of \( s_{RF} \). The line is a linear fit to the data points.
Chapter 5: InP: ESR and Overhauser Spectroscopy

Fig. 5.13: Overhauser shift as a function of RF power for $^{115}$In nuclei at 8K and $P_{\text{RF}}=34\,\text{dB}(0.08\,\text{mW})$. The function used for fitting is of the form $y = A \beta x / (1 + \beta x)$. The measured Overhauser shift is shown as a function of $s_{\text{RF}}$ in the inset. The line is a linear fit to data points.

In order to investigate if the nuclear spin lattice relaxation time depends on RF power, the $^{115}$In Overhauser measurements at different RF power were fit with an exponential decaying function. It was observed that at high RF power, the data could not be fitted with a single monoexponential function. A function of the form $y = A \exp(-t/T_1^*)$, known as a stretched exponential relaxation function, was used for the fitting. It is shown in fig 5.14.

The stretched exponential relaxation is commonly encountered in systems where many independent relaxing species occur, each of which decays exponentially in time with a specific fixed relaxation rate ($\lambda$). The stretched exponential function can then be written in the form of a sum of pure exponential decays with a probability distribution of $\lambda$. In the case of InP measurements, this function can be interpreted by considering the shallow donor picture. As discussed in section 2.1, shallow donors in InP have extended wavefunctions. The strength of the Fermi contact hyperfine interaction experienced by nuclei within this extended wavefunction depends on the distance from the donor centre.
Since these nuclei relax mainly via the electrons, the $T_1$ of the nuclei depends on the distance from the donor. The $T_1$ measured (referred to as $T_1^*$) is thus a resultant of the contributions from various sets of nuclei with different relaxation rates and follows the stretched exponential relaxation behaviour. The parameter $\eta$ represents the degree of inhomogeneity in the system. For $\eta = 1$, the relaxation is a pure mono-exponential type typical for a system where all the nuclei have the same relaxation rate. In case of $^{115}$In, fittings were done for measurements at different RF power and $\eta$ was determined. Fig 5.15 shows the variation of $\eta$ with respect to RF power. At very low RF power, $\eta \approx 1$. As RF power is increased, $\eta$ increases (linearly). At low RF power, only the nuclei which are weakly coupled to the donor electron can be depolarized. As the RF power is increased, even the strongly coupled nuclei (close to the donor) can be depolarized leading to a distribution in $T_1$ and hence an increase in $\eta$. $T_1^*$ as a function of $P_{RF}$ is shown in fig.5.16. The average value of $T_1^*$ is comparable to that obtained from line position measurements described in section 5.2.

![Graph showing Overhauser shift vs. radiofrequency curve for $^{115}$In at 8K. The fitting to the data after $f_{res}$ is done by a function: $y = A \exp(-x/T_1^*)^\eta$](image)

**Fig.5.14:** Overhauser shift vs. radiofrequency curve for $^{115}$In at 8K. The fitting to the data after $f_{res}$ is done by a function: $y = A \exp(-x/T_1^*)^\eta$. Sweep time is 1200s. $P_{RF}=1mW$, $P_{\mu_0}=34dB (0.08mW)$
Fig. 5.15: Stretched exponential function parameter ($\eta$) as a function of RF power for $^{115}\text{In}$ measurements at 8K.

Fig. 5.16: $T_1^*$ (obtained from stretched exponential function fitting) as a function of RF power for $^{115}\text{In}$ measurements at 8K.
Fig. 5.17 shows the Overhauser shift as a function of RF power for $^{31}$P. Although, the recovery of ESR line position follows a mono-exponential decay function for any RF power used, the plot of Overhauser shift vs. RF power could not be fit with equation 5.9. For proper fitting of the measured data points, an expression of the form equation 3.10 was used.

$$ B_n(P_{RF}) = B_{n1} \cdot \frac{\beta_1 P_{RF}}{1 + \beta_1 P_{RF}} + B_{n2} \cdot \frac{\beta_2 P_{RF}}{1 + \beta_2 P_{RF}} $$  \hspace{1cm} (5.10) 

This is again a characteristic of a system with more than one type of nuclei which relax independently with their own $T_1$. Since the S/N ratio for $^{31}$P measurements is not very good, using two RF saturation factors ($\beta_1$ and $\beta_2$) gives a reasonable fit to the measured data.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{overhauser_shift_graph.png}
\caption{Overhauser shift as a function of RF power for $^{31}$P nuclei at 8K and $P_{\mu\omega}=34$dB(0.08mW). The function used for fitting is of the form $y = A \cdot \frac{\beta_1 x}{1 + \beta_1 x} + B \cdot \frac{\beta_2 x}{1 + \beta_2 x}$}
\end{figure}
**Conduction Electron Wave Function**

Another interesting aspect of Overhauser technique is that the density of conduction electron at a particular nuclear site can be determined from the measured Overhauser shift. This is explained in the following section.

As described in section 5.6, the nuclear field experienced by electrons is given by

$$B_n = \frac{A\langle I_Z \rangle}{g^* \mu_B}$$  \hspace{1cm} (5.11)

where $g^*$ is the effective $g$ factor of the electron and $A$ is the Fermi contact hyperfine interaction given by

$$A = \frac{8\pi}{3} \frac{\mu_0}{4\pi} g \mu_B h \gamma_n |\psi(0)|^2$$  \hspace{1cm} (5.12)

where $g=2.0023$ is the $g$-factor of the free electron, $\gamma_n$ is the gyromagnetic ratio of the nucleus, $\mu_0$ is the permeability of free space and $|\psi(0)|^2$ is the density of conduction electrons at the nuclear site. In thermal equilibrium at temperature $T$, $\langle I_Z \rangle$ is given by

$$\langle I_Z \rangle \approx \frac{h \gamma_n I(I+1)}{3kT}$$  \hspace{1cm} (5.13)

where $I$ is the nuclear spin quantum number. Equation (5.13) is valid for $h \gamma_n B = \frac{kT}{kT} \ll 1$ which is true down to mK range. From equations (5.11), (5.12) and (5.13), the nuclear field may be written as:

$$B_n = \frac{4\mu_0 (h \gamma_n)^2 I(I+1)}{9kT g^*} |\psi(0)|^2 B$$  \hspace{1cm} (5.14)

Thus by measurement of the relative shift $D = B_n/B$ for a particular type of nuclei, the conduction electron density at that nuclear site can be determined. The parameters obtained for $^{115}$In and $^{31}$P nuclei are summarized in table 5.2.

**Table 5.2. Overhauser Shift parameters obtained for InP at 8K**

| Nucleus | $\gamma$(Ts)$^{-1}$ | $I$ | $T_1$(s) | $D_0$(ppm) | $|\psi(0)|^2$(cm$^{-3}$) |
|---------|-----------------|---|---------|--------|----------------|
| $^{115}$In | $5.863 \times 10^7$ | $9/2$ | 105 | 286 | $6.79 \times 10^{25}$ |
| $^{31}$P | $10.83 \times 10^7$ | $1/2$ | 175 | 13 | $3.18 \times 10^{25}$ |
Chapter 5: InP: ESR and Overhauser Spectroscopy

The values of $|\psi(0)|^2$ obtained from these measurements can be compared to the atomic values taken from$^{80}$. The electron densities in InP are reduced to 72% and 65% of the atomic values respectively for $^{115}$In and $^{31}$P nuclei. Such a reduction in electron density with respect to the pure s-type atomic values is generally observed in metals and InSb$^{81,82,83}$. Also, the conduction electron is unequally shared between In and P, with enhanced probability at In nucleus.

**Paramagnetic Shift**

A careful look at Overhauser profile of $^{115}$In nuclei (fig. 5.18) shows that the Overhauser signal line shape is not a step function at the nuclear resonance frequency. Instead, a broadened and asymmetric lineshape is obtained at sweep frequency lower than the resonance frequency. This broadening is the result of shift of nuclear resonance frequency due to influence from the electron (paramagnetic shift). From fig. 5.18 the paramagnetic shift of $^{115}$In may be estimated to be $\sim 20$kHz at 8K. Similar asymmetry in NMR lineshapes and paramagnetic shift comparable to our observations have been reported in the literature$^{84}$ in n-type InP.

![Fig.5.18: Overhauser shift vs. radiofrequency for $^{115}$In at 8K. The broadened and asymmetric lineshape is due to paramagnetic shift of $^{115}$In nuclei.](image)
5.4 DNP in InP

As explained in section 5.2, the Overhauser enhancement factor \( V \) depends on the gyromagnetic ratios of the electron and the nucleus and a “leakage” factor \( f \):

\[
V = \frac{g^* \mu_B}{\hbar \gamma_n} \cdot f
\]  

(5.15)

If the nuclei relax only via the isotropic hyperfine interaction, \( f = 1 \) and the nuclear spin polarization would be enhanced by a factor

\[
V_{\text{max}} = \frac{g^* \mu_B}{\hbar \gamma_n}.
\]  

(5.16)

where \( g = 2.0023 \) is the \( g \)-factor of the free electron and \( \gamma_n \) is the gyromagnetic ratio of the nucleus. In case of InP, this would mean the nuclear polarization of \(^{115}\text{In}\) and \(^{31}\text{P}\) are enhanced by a factor of 1796 and 977 respectively. There are however other processes by which the nuclei relax such as quadrupolar relaxation and relaxation via paramagnetic impurities. The leakage factor in such cases is defined by the ratio of relaxation rate via the contact hyperfine interaction \( w_c \) to the total relaxation rate \( 1/T_1 = w_c + w_i \) where \( w_i \) is the relaxation rate due to processes other than the contact hyperfine interaction. The enhancement factors were measured for \(^{115}\text{In}\) and \(^{31}\text{P}\) by recording the Overhauser shift as a function of microwave power (section 5.3) and leakage factors were deduced from that. The DNP parameters for both the nuclei are summarized in table 5.3. \(^{115}\text{In}\) has a much smaller leakage factor as compared to \(^{31}\text{P}\) since the relaxation rate \( w_i \) is larger for \(^{115}\text{In}\) as compared to \(^{31}\text{P}\). This is expected since \(^{115}\text{In}\) is a 9/2 nucleus and hence undergoes quadrupolar relaxation even at low temperatures, whereas no quadrupolar relaxation is possible for \(^{31}\text{P}\) (spin 1/2 nucleus). This has been confirmed by our \( T_1 \) measurements described in chapter 4.

Table 5.3. Dynamic nuclear polarization parameters obtained for InP at 8K

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>( V_{\text{max}} )</th>
<th>( V )</th>
<th>( f )</th>
<th>1000( w_c ) (s(^{-1}))</th>
<th>1000( w_i ) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{115}\text{In})</td>
<td>1796</td>
<td>257</td>
<td>0.143</td>
<td>2.15</td>
<td>7.85</td>
</tr>
<tr>
<td>(^{31}\text{P})</td>
<td>977</td>
<td>454</td>
<td>0.465</td>
<td>2.66</td>
<td>3.05</td>
</tr>
</tbody>
</table>
5.5 ESR in GaAs

GaAs is one of the most widely used and studied semiconductor in electronics industry, second only to silicon. Spin dependent properties of conduction band states in this material, however, still remain rather poorly determined. ESR spectroscopy which provides a direct and easy access to information about spin properties is not very suitable on GaAs since the expected resonance field falls out of the range of standard ESR spectrometers. Therefore, our present knowledge of spin-dependent properties in this material has been established on the basis of indirect measurements such as optical pumping experiments in bulk\textsuperscript{37,60,61} as well as heterostructures\textsuperscript{85,43}, cyclotron resonance measurements\textsuperscript{86} and electrically detected resonance\textsuperscript{87}. These measurements combined with theoretical models provide an estimation of electron g factor (-0.44 ± 0.02 in the bulk). Moreover, optical pumping experiments have highlighted the importance of hyperfine coupling of electron spins to nuclear spins (an effective hyperfine field of up to 5.3T can be expected\textsuperscript{41} in GaAs).

The only instance of direct ESR measurement\textsuperscript{88} on bulk GaAs has been the ESR on shallow donor electrons in low doped n-type GaAs (2.6×10\textsuperscript{14}cm\textsuperscript{-3} ≤ n ≤ 2.7×10\textsuperscript{15}) at high magnetic fields (6-11T). Highly asymmetric and broad (∼0.5T) ESR lineshapes strongly dependent on the magnetic field sweep direction have been reported.

We performed standard ESR measurements on nGaAs (sample #3) with doping concentration 1.2×10\textsuperscript{15}cm\textsuperscript{-3} using a broadband (5-40GHz) ESR spectrometer combined with a superconducting magnet (up to 10T). The transmission from the ESR cavity was measured as a function of magnetic field at 1.6K. Fig. 5.19(a) and (b) show the transmission vs. magnetic field curves at two different microwave powers. A broad ESR line (∼0.4T) was observed at \(g_\text{e}=-0.4215\) at 1μw microwave power. At higher microwave power (2μW), a much broader ESR line (1T) was observed. This broadening of the ESR line is due to Overhauser shift induced by dynamic nuclear polarization. This is similar to the line-broadening observed in InP measurements described earlier in this chapter. In order to minimize the broadening effects, one must prevent Overhauser effects by sweeping the magnetic field very fast across the ESR line. This was not possible in our set up due to limitation of magnetic-field sweep rate of the superconducting magnet.
Chapter 5: InP: ESR and Overhauser Spectroscopy

4.4 4.8 5.2 5.6 6.0 6.4

0.0187
0.0188
0.0189
0.0190
0.0191
0.0192

Transmission

Magnetic Field (T)

ge=-0.4215

(a)

Fig. 5.19: Cavity transmission as a function of magnetic field with n-GaAs (sample #3) at 1.6K at (a) $P_{\mu W} = 1\mu W$ and (b) $P_{\mu W} = 2\mu W$.

(b)

Fig. 5.19: Cavity transmission as a function of magnetic field with n-GaAs (sample #3) at 1.6K at (a) $P_{\mu W} = 1\mu W$ and (b) $P_{\mu W} = 2\mu W$. 
Owing to the broad and asymmetric ESR lines and practical limitations of the ESR set-up, it was not feasible to perform a precise measurement of Overhauser shift in this sample. However, the asymmetry of ESR lines and its dependence on microwave power clearly indicates that strong hyperfine coupling (and hence DNP) exists in low doped GaAs. Optically oriented and detected ESR measurements in GaAs with similar doping also point in the same direction (Overhauser shifts ~60G have been reported in literature\textsuperscript{89}).

5.6 Conclusion and Outlook

Our extensive Overhauser shift measurements on InP and preliminary ESR experiments on GaAs have underlined the importance of electron nuclear hyperfine coupling in both these semiconductors. At low temperatures and at low doping concentration levels, huge DNP enhancements have been observed. Furthermore, we see that the nuclear spin lattice relaxation time measured by Overhauser technique is much shorter than the bulk T\textsubscript{1} values mentioned in Chapter 4. This highlights the role of localized donor centres in DNP processes and the presence of strong hyperfine coupling experienced by nuclei in proximity to electron centres.

Having shown that DNP can be induced by microwave saturation in InP and GaAs at low temperatures and at low doping concentrations, we attempt to investigate other mechanisms of creating DNP in these semiconductors. As described in Chapter 2, crystals with zinc-blende structure lack inversion symmetry and exhibit current induced electron spin polarization. CISP has been experimentally observed in GaAs\textsuperscript{24,25,27}. We thus expect both InP and GaAs to show current induced dynamic nuclear polarization. Experiments to investigate the effect of electric current on nuclear polarization in low doped InP and GaAs are discussed in chapter 7. In the next chapter, Overhauser measurements on another interesting semiconductor system (phosphorus doped silicon) are described.
Chapter 6

Si:P: ESR and Overhauser Spectroscopy

First ESR studies\textsuperscript{90,91} of bound donor electrons in silicon were performed as early as 1954. Since then, phosphorus doped silicon has been one of the most extensively studied semiconductors with respect to electron and nuclear spin related properties. Magnetic resonance has proved to be a very useful tool to investigate the changes of electronic structure across the metal insulator transition\textsuperscript{92}. Several recent proposals\textsuperscript{93,32} of a silicon based quantum computer have led to a renewed interest in investigations of spin dependent phenomena in this material. Phosphorus donors in silicon are spin $\frac{1}{2}$ nuclei with long spin relaxation time\textsuperscript{94,95}. Thus, they present themselves as a nearly perfect two level system suitable for constituting a quantum bit. Detection of nuclear spins with high sensitivity however is an obstacle in the way of realization of nuclear spin based quantum computation. An attractive alternative approach is to manipulate and detect nuclear spins electronically\textsuperscript{96,97} via the strong hyperfine interaction\textsuperscript{94} between electron and nuclear spins. Spin polarization is transferred between the two spin systems and nuclear spin polarization is detectable by its effect on the electronic properties\textsuperscript{98,99} of the sample. This transfer of polarization from electron spins to nuclear spins (dynamic nuclear polarization) and vice versa has emerged as an interesting area of research where various groups worldwide have been involved in recent years\textsuperscript{100,101,102}. The hyperfine interaction of the localized donor electron with $^{29}$Si nuclei was investigated by Feher\textsuperscript{94} in a sample with $n \ll n_c$ (where $n_c$ is the doping
concentration at metal-insulator transition) by means of classical ENDOR technique. For such low donor concentration, the donor electrons are isolated and the ESR line is split into two lines by HFI with the central P nucleus. At concentration higher than about $1 \times 10^{18} \text{cm}^{-3}$, the strong exchange interaction between nearest neighbor electron spins leads to a single exchange narrowed line. In such a scenario, ENDOR is not possible. Study of HFI by means of standard NMR experiments is also not possible due to small natural abundance of $^{29}\text{Si}$ nuclei and also due to the fact that the NMR signal is dominated by the Si nuclei in the bulk. Overhauser shift technique, thus, provides a unique possibility to investigate HFI in such systems.

We investigated dynamic nuclear polarization in phosphorus doped silicon with a donor concentration of about $3 \times 10^{18} \text{cm}^{-3}$ by means of Overhauser technique described in the previous chapter. The ESR experiments were performed with a commercial X-Band (10GHz) ESR spectrometer (Bruker). Low temperature measurements were done using a continuous flow liquid helium cryostat (Oxford Instruments) and temperature controller (Oxford Instruments, ITC4). All experiments reported were carried out at 8K or 10K.

6.1. ESR Spectra

The ESR spectrum obtained from this sample shows a very narrow line with Dysonian lineshape typical for conducting samples. ESR lines at 10K and different microwave powers are shown in fig.6.1. The lines can be fitted by a superposition of absorption and dispersion parts of 1st derivative of a lorentzian function. From the fitting parameters the degree of dispersion, line position and line width can be obtained to a high precision.

It was observed that the degree of dispersion increases with increase in microwave power. Since our samples are thicker than the skin depth, the asymmetry may be caused by the phase shift and damping of the microwave field on its way to the sample. A similar asymmetric lineshape was however seen in the previous study as well for samples much thinner than the skin depth. In such thin samples, the increase in asymmetry with increasing ESR saturation was explained by considering regions with different hyperfine interactions in the samples and thus different Overhauser shifts (due to statistical distribution of donor atoms). Our samples thus appear to exhibit a combination of these two effects due to microwave phase shift and inhomogenous Overhauser shift.

The ESR linewidth was also observed to be microwave power dependent. Linewidths vary from 400mG to 850mG for microwave power variation
from 0.2 to 200mW. This dependence is again a result of two independent factors contributing to the ESR linewidth, namely the line width increase with ESR saturation and inhomogenous broadening of the ESR line due to Overhauser shift.

From the fitting of the ESR line, the exact line position was obtained at different microwave powers. With careful analysis and after eliminating the effects of frequency and magnetic field drifts, it was observed that the ESR line position shifts to lower magnetic field with increase in microwave power. This is shown in fig. 6.2. This shift of the ESR line position with increase in microwave power is the integral Overhauser shift (net Overhauser shift due to Si and P nuclei) A total shift close to 160mG is observed for $P_{\mu w} = 65$mW at 8K. This value compares well with
the shift of 150mG measured by Fasol et al\textsuperscript{104} in a sample with $n = 3.55 \times 10^{18}$ cm\textsuperscript{-3}. The plot of ESR line position vs. microwave power upon extrapolation to $P_{\mu w}=0$ gives the true line position (and hence the true g-factor) without any effect from the surrounding nuclei. Data points in fig.6.2 are fitted with a function of the type described by eqn.5.5 to obtain the true g-factor as 1.9998.

Since the ESR line is shifted to smaller fields with increasing ESR saturation, this means that the dominant hyperfine field has a positive sign. The two nuclei responsible for the shift ($^{29}$Si and $^{31}$P) have opposing effects on the ESR line position due to opposite sign of gamma ($\gamma_{Si}<0$ and $\gamma_{P}>0$). The negative sign of the line shift indicates increasing positive hyperfine field. Thus, the contribution from $^{31}$P nuclei is much stronger than the $^{29}$Si nuclei. This is expected since the electron wavefunction density (and hence the HFI) is the strongest at the central nucleus and drops off exponentially as the distance from the donor is increased. In order to separate the effects from two nuclei, their respective nuclear polarization has to be destroyed separately by doing a double resonance type of measurement. This is described in the next section.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig6.2.png}
\caption{Si:P ESR line position as a function of microwave power at 8K. $\Delta B=160$mG, $f_{\mu w}=9.771584$ GHz. Fitting with a function: $B(P_{\mu w}) = B(0) + bcP_{\mu w}/(1+cP_{\mu w})$ where $B(0)=3490.80225$, $b=-0.40674$ and $c=0.01028$mW\textsuperscript{-1}}
\end{figure}
6.2 Overhauser Shift Measurement by Double Resonance

Overhauser shift measurements were performed on phosphorus doped silicon by means of double resonance technique described in section 5.3. Fig 6.3 shows a typical Overhauser shift vs. radiofrequency curve for Si nuclei. It is to be noted that the signal is inverted (shift towards negative field) as compared to the InP signal due to negative $\gamma$ of $^{29}$Si nuclei.

In principle, the dynamic nuclear polarization can build up via anisotropic dipolar as well as isotropic Fermi contact hyperfine interaction. The polarization resulting from these two types of interactions however have opposing signs. The negative sign of the Overhauser shift by $^{29}$Si nuclei clearly shows that the Fermi contact hyperfine interaction is the dominant interaction responsible for dynamic nuclear polarization of $^{29}$Si.

![Fig. 6.3: A typical Overhauser measurement spectrum at 10K, $P_{\text{rf}}=63.2$ mW $P_{\text{rf}}=19.5$ mW. The asymmetric part after the $^{29}$Si NMR frequency is fitted by a biexponential curve of the form: $B_n = B_{\text{on}} \left\{ \exp(-f_1 / f_1) + \exp(-f_2 / f_2) \right\}$ where $f_1=16.3$ kHz and $f_2=1.27$ kHz. The asymmetric lineshape of the signal is due to the distribution of distance of $^{29}$Si nuclei from P donors leading to a distribution in hyperfine interaction (and hence the Overhauser shift and the paramagnetic shift). As was described in section 3.3, the strength of Fermi contact hyperfine interaction experienced by nuclei within donor wavefunction depends on the distance from the donor centre. The nuclei...](image-url)
closest to the donor centre experience maximum hyperfine interaction and thus create maximum Overhauser shift. The strong hyperfine interaction however also shifts the nuclear resonance frequency (paramagnetic shift) towards higher frequency resulting in the extended part of the Overhauser signal. The nuclei far away from the electron centre experience less hyperfine interaction and have lower frequency shifts. These far away nuclei are however much more in abundance ($r^2$ dependence) and thus have much higher contribution to the Overhauser shift resulting in a strong negative dip in the Overhauser signal. A schematic diagram of the type of nuclei contributing to different parts of the Overhauser signal is shown in fig. 6.4.

Fig.6.4: A schematic diagram of the type of nuclei contributing to different parts of the Overhauser signal.
A similar asymmetric lineshape has been seen in NMR measurements reported in the literature\textsuperscript{106,107}. It was seen that the high frequency side of the NMR signal has a long tail and is broadened. The broadening and asymmetry of NMR line is less than that in the Overhauser line due to the fact that NMR measures bulk nuclei whereas the Overhauser measurement technique selectively picks out nuclei close to electron centres.

In our measurements it was observed that the high frequency side of the Overhauser signal could be fitted reasonably by a biexponential function of the form:

\[ B_n = B_{n0} \{ \exp(-f / f_1) + \exp(-f / f_2) \} \]

where \( f_1 \) and \( f_2 \) are fitting parameters in units of frequency. The system being studied here has a distribution of nuclear resonance frequencies. Such systems can usually be described reasonably by a two level system corresponding to resonance frequencies \( f_1 \) and \( f_2 \). The difference between the fitting parameters \( (f_1 \) and \( f_2 \) gives an estimate of the distribution of frequencies. The larger the difference between \( f_1 \) and \( f_2 \), the greater is the extent of distribution. The dependence of the frequency distribution on RF power was studied and is described in the next section.

**RF Dependence**

The increase in RF power at a fixed ESR saturation affects the Overhauser signal in two different ways:

(i)\textbf{Saturation Effect:} The extreme of the signal (negative dip) increases with increase in RF power initially and shows a saturation kind of behavior with respect to RF power. The Overhauser shift is plotted as a function of RF power in fig.6.5.

As described in section 5.3, the dependence of measured Overhauser shift on RF power follows a relation:

\[ B_n(P_{RF}) = B_n \cdot s_{RF} \]

\[ s_{RF} = \frac{(\gamma_n B_2)^2 T_1 T_2}{1 + (\gamma_n B_2)^2 T_1 T_2} \]

Fitting of the data points in fig 6.5 with a function of the form

\[ B_n(P_{RF}) = B_n \cdot \frac{\beta P_{RF}}{1 + \beta P_{RF}} \]
Fig. 6.5: Overhauser shift as a function of RF power for $^{115}\text{In}$ nuclei at 8K and $P_{\mu W}=34\text{dB}(0.08\text{mW})$. The function used for fitting is of the form $y = A\beta x/(1 + \beta x)$.

(ii) The second effect of increasing RF power is on the fitting parameters $f_1$ and $f_2$. At low RF power, the measured Overhauser shift comes from a distribution of nuclei at various distances from the donor electron. This distribution can be fitted by a biexponential curve. The nuclei close to the donor electron have very short $T_1$ times and hence are difficult to saturate. As the RF power is increased, these nuclei can be saturated resulting in an enhancement of high frequency wings of the Overhauser profile. This leads to an approximate monoexponential fitting of Overhauser profile ($f_1$ and $f_2$ converge to a single point at high RF power, seen in fig. 6.6).
Fig. 6.6: $f_1$, $f_2$ obtained from biexponential curve $B_n = B_{n0} \left\{ \exp(-f/f_1) + \exp(-f/f_2) \right\}$ as a function of RF power at 10K.

**ESR Saturation Dependence**

The dependence of Overhauser shift on microwave power is given by (refer to eqn. 5.6)

$$B_n = B_{n0} \left[ 1 + \frac{V \alpha P_{\mu W}}{(1 + \alpha P_{\mu W})} \right]$$

where $B_n$ is the Overhauser shift, $B_{n0}$ is the thermal equilibrium value of the Overhauser shift, $V$ is the Overhauser enhancement factor which depends on the gyromagnetic ratios of the electron and the nucleus and a “leakage factor” $f$. In order to determine the DNP parameters ($B_{n0}$, $V$ and $f$) for Si:P sample, the dependence of the Overhauser shift on ESR saturation was measured. This is shown in fig. 6.7.
By fitting this curve with a function of the form

\[ B_n = B_{n0} \left[ 1 + \frac{V\alpha P_{\mu W}}{1 + \alpha P_{\mu W}} \right] \]

we obtain the DNP parameters: \( \alpha = 4.59 \times 10^{-2} \text{ mW}^{-1} \), \( B_{n0} = -0.124 \text{ mG} \) and \( V = -31.2 \). Using this value of \( \alpha \), the ESR saturation factor \( s_{esr} \) is obtained. Fig. 6.8 shows Overhauser shift as a function of \( s_{esr} \).

---

Fig. 6.7: Overhauser shift as a function of microwave power for \( ^{29}\text{Si} \) nuclei at 10K

Fitting with a function \( B_n = B_{n0} \left[ 1 + \frac{V\alpha P_{\mu W}}{1 + \alpha P_{\mu W}} \right] \) where \( \alpha = 4.59 \times 10^{-2} \text{ mW}^{-1} \), \( B_{n0} = -0.124 \text{ mG} \) and \( V = -31.2 \).
Fig. 6.8: Overhauser shift as a function of ESR saturation factor for $^{29}$Si nuclei at 10K. Extrapolation to $P_{\mu w}=0$ gives $B_{n0}=-0.124\text{mG}$ ($D_0=B_{n0}/B=0.0356\text{ppm}$)

**Knight Shift/Paramagnetic Shift**

Apart from the measurement of the shift of the ESR line position due to the influence of nuclei, the Overhauser measurement technique allows precise measurement of nuclear resonance frequency as well. As seen from fig.6.3, a sharp peak in the Overhauser measurement signal is observed when the sweep radio frequency reaches the resonance frequency of the nuclei. Nuclear resonance frequency and the shift of NMR frequency due to hyperfine interaction with electrons (Knight shift) can thus be measured by this technique. This is particularly useful in samples with low doping concentration since direct Knight shift measurements are not possible in such samples due to dependence of Knight shift on electron concentration.

Nuclear resonance frequencies were determined at different ESR saturation levels using this measurement technique. Since the NMR position is unaffected by electrons at $s_{\text{efr}}=1$, the shift of NMR frequency with respect to frequency at $s_{\text{efr}}=1$ gives the Knight shift. Fig 6.9 shows the Knight shift as a function of ESR saturation. Our measured Knight shift is about two orders of magnitude greater than the values reported
in literature\textsuperscript{106}. This is due to the fact that the Overhauser measurement technique selectively picks out the nuclei close to localized donors. These nuclei experience strong hyperfine coupling with the donor electron leading to large shift of their resonance frequency. This shift is known as the paramagnetic shift (or as Knight shift due to conduction electrons). NMR measurements, on the other hand, measure predominantly the bulk nuclei which are not affected by localized electrons.

\begin{center}
\includegraphics[width=\textwidth]{fig6_9.png}
\end{center}

\textbf{Fig. 6.9: }\textsuperscript{29}Si Knight shift as a function of ESR saturation factor at 10K. Linear fitting is done by function: \( y=a+bx \) where \( a=1.19 \) and \( b=-711.83 \).

\section*{Conduction Electron Wave Function}

From the measurement of Overhauser shift due to a particular nucleus, the conduction electron wavefunction density at that nuclear site can be determined. This was described in detail in section 5.3. From eqn. 5.14 we have:

\[
B_n = \frac{4\mu_0(h\gamma_n)^2 I(I+1)}{9kTg^*} |\psi(0)|^2 B
\]

where \( B_n \) is the measured Overhauser shift, \( B \) is the external magnetic field, \( g^* \) is the effective \( g \) factor of the electron, \( \gamma_n \) is the gyromagnetic ratio.
of the nucleus, $\mu_0$ is the permeability of free space and $|\psi(0)|^2$ is the density of conduction electrons at the nuclear site. Using the measured Overhauser shift values, the electron wavefunction density at $^{29}\text{Si}$ nuclear site was calculated to be $7.45 \times 10^{23} \text{cm}^{-3}$. This is comparable to the values reported in literature\cite{94,108} ($n = 1.16 \times 10^{24} \text{cm}^{-3}$).

### 6.3 DNP in Si:P

For the case of dynamic nuclear polarization created by isotropic hyperfine interaction, the maximum possible DNP enhancement for a nuclear system is given by the ratio of the electron and nuclear gyromagnetic ratio. In the case of Si:P, maximum enhancement factor for $^{29}\text{Si}$ nuclei is:

$$V_{\text{max}} = \frac{g^* \mu_B}{\hbar \gamma_n} = -3305.$$  

This situation is realized when the only possible channel of nuclear relaxation is via electrons. In presence of other modes of nuclear relaxation, the enhancement factor is given by:

$$V = \frac{g^* \mu_B}{\hbar \gamma_n} \cdot f$$

where $f$ is the leakage factor. From our measurements, the leakage factor is determined to be $f = V/V_{\text{max}} = 0.009$. Thus, in this sample, only 1% of nuclear spin lattice relaxation originates from the conduction electrons.

### 6.4 Overhauser Shift Measurement on Central Nucleus

As has been pointed out already, the strongest hyperfine interaction is experienced by nuclei closest to the electron centre. Thus, the central nucleus ($^{31}\text{P}$ in this case) is strongly coupled to the electron. This poses a problem in detection of central nucleus due to extremely short relaxation time. In order to saturate the NMR transition of the central nucleus, strong RF fields and a high quality factor of the cavity is needed. Since the Overhauser signal is very small, high stability of field as well as temperature is also essential.

Overhauser shift due to central nucleus can however be estimated from the integral shift (shown in fig. 6.2) and the measured $^{29}\text{Si}$ shift (fig. 6.7). Since $^{29}\text{Si}$ and $^{31}\text{P}$ nuclei shift the ESR line in opposite directions (due to different signs of nuclear $\gamma$), contribution of $^{31}\text{P}$ nuclei can be deduced by adding the measured $^{29}\text{Si}$ contribution to the measured integral shift.
This is shown in fig. 6.10. The data points are fitted with an expression:

\[ B_n - B_{n0} = B_{n0} \left( \frac{V\alpha P_{\mu W}}{1 + \alpha P_{\mu W}} \right) \]

From the fitting parameters the value of \( \alpha \) and the product \( (B_{n0} \cdot V) \) are obtained for \(^{31}\text{P}\) nuclei as \( \alpha = 9.27 \times 10^{-3} \) mW\(^{-1}\) and \( B_{n0} \cdot V = -435.8 \) respectively. Overhauser shift vs. \( s_{\text{esr}} \) is plotted in fig 6.11. It is to be noted that the shift measured by this technique is \( (B_n - B_{n0}) \) and not \( B_n \). In order to measure the Overhauser shift due to \(^{31}\text{P}\) nuclei at thermal equilibrium \( (B_n) \), the nuclear spin polarization must be reduced to zero. This can be achieved only by double resonance experiments. Thus, this technique of indirect measurement of \(^{31}\text{P}\) Overhauser shifts does not allow determination of the DNP enhancement factor \( (V) \) for \(^{31}\text{P}\) nucleus.

Fig. 6.10: Shift of ESR line as a function of microwave power for \(^{31}\text{P}\) nuclei at 10K. Fitting with a function \( y = A\alpha z/(1 + \alpha z) \) where \( \alpha = 9.27 \times 10^{-3} \) and \( A = -435.8 \text{mG} \).
Fig. 6.11: Shift of ESR line due to $^{31}$P contribution as a function of ESR saturation parameter. Linear fit of the data points gives slope = -435.8

From Fig. 6.10 and 6.11, the ESR line shift at complete ESR saturation ($s_{esr}=1$) is obtained to be 435.8 mG. Since the Overhauser shift due to $^{31}$P nuclei at thermal equilibrium ($B_n$) is expected to be much smaller than shift at complete saturation ($s_{esr}=1$), one may assume $(B_n - B_{n0}) \approx B_n = 435.8$ mG. Furthermore, one can estimate the expected $^{31}$P Overhauser shift numerically. In contrast to Overhauser Shift due to $^{29}$Si nuclei, the contribution from central nucleus ($^{31}$P in this case) is easy to compute. The nuclear field at the central nucleus is given by:

$$B_n = A\langle I \rangle / (g \mu_B)$$

where

$$A(r) = \left( \frac{8\pi}{3} \right) \cdot \left( \frac{\mu_B}{4\pi} \right) \cdot g\mu_B \hbar \gamma_n |\psi(0)|^2$$

and

$$\psi(r) = \frac{1}{\sqrt{\pi a_{eff}^3}}$$

Using $a_{eff} = 13.45$ Å$^{109}$, one gets $B_n = 6.24$ mG. This value is about 2 orders of magnitude smaller than the measured Overhauser shift at complete
ESR saturation (435.8 mG). This mismatch of experimental and calculated values clearly points out the importance of core factor (C) in computation of hyperfine interaction. The physical importance of core factor and its necessity in such calculations is described in detail in section 2.1 and 7.2. Here we simply point out the fact that the hyperfine interaction calculated using EMT agrees well with the experimental values only when an amplification factor (C=435.8/6.24~70) is included in the calculation of the hyperfine interaction.

6.5 Outlook

Standard techniques of semiconductor doping usually result in a non uniform distribution of donor or acceptor impurities. We have seen the effects of non uniform doping on electron-nuclear hyperfine interactions in Overhauser measurements on InP as well as Si:P. A particularly interesting study would be the Overhauser shift spectroscopy in semiconductors with uniform impurity distribution. A promising method of obtaining such doping in semiconductors is neutron transmutation doping (NTD). This method has been used extensively for preparation of extremely uniform n-Si films for fabrication of high-power devices. Transmutational doped and $^{30}$Si enriched silicon crystals have already been studied by means of standard electron spin resonance spectroscopy$^{110}$. However, no double resonance measurements on such sample have been performed till date. Our technique of measuring Overhauser shift when used on such uniformly doped Si crystals would open a possibility of investigating precisely the electron-nuclear hyperfine interaction by alleviating the effects induced by donor wavefunction overlap.
Chapter 7

Modeling and Simulations

In order to understand the interactions which are responsible for creation of dynamic nuclear polarization and Overhauser shifts in semiconductors, a quantitative model was developed using MATLAB. This is described in this chapter.

We consider a semiconductor (n-type) with homogenous and low doping concentration such that the donor electron wavefunctions do not overlap. It is to be noted that this is a simplified picture since the doping of semiconductors is never homogenous due to the tendency of donor atoms to form clusters. Thus, the overlap of donor wavefunctions can almost never be avoided. This simplified picture is, however, sufficient to obtain a qualitative model to describe such a semiconductor sample.

7.1 Electron Wavefunction

As explained in detail in section 2.1, the electron wavefunction of a localized donor can be described by effective mass theory as:
Chapter 7: Modeling and Simulations

\[ \varphi(r) = \frac{1}{\sqrt{\pi a_{\text{eff}}^3}} \exp\left(-\frac{r}{a_{\text{eff}}}\right) \]  \hspace{1cm} (7.1)

where

\[ a_{\text{eff}} = \frac{4\pi \varepsilon_0 \varepsilon_r \hbar^2}{m_{\text{eff}} e^2} = \frac{\varepsilon_r m_0}{m_{\text{eff}}} a_0 \]

In case of InP, \( \varepsilon_r = 12.5, \frac{m_{\text{eff}}}{m_0} = 0.077 \) and thus \( a_{\text{eff}} = 85 \text{ Å} \) (8.5nm).

Going away from the position of the donor, the wavefunction falls off exponentially. The contribution of the nuclei at distance \( r \) from the donor depends on the product of electron density and the number of nuclei at \( r \). This is represented as:

\[ f(r) = |\varphi(r)|^2 \cdot 4\pi r^2 \]

From fig.7.1, it is seen that the nuclei at \( r = \text{Bohr radius} \) (= 8.5nm) give a maximum contribution to the Overhauser signal.

![Fig. 7.1: Extended wavefunction of donor electron as per effective mass theory.](image-url)
7.2 Contact Hyperfine Interaction

Knowing the density of electron wavefunction at radius \( r \), the strength of Fermi contact type hyperfine interaction experienced by a nucleus at \( r \) can be calculated from the following relation:

\[
A(r) = \left( \frac{8\pi}{3} \right) \cdot \left( \frac{\mu_0}{4\pi} \right) \cdot g\mu_B \hbar \gamma_n |\psi(r)|^2
\]  

(7.2)

The strength of hyperfine interaction is thus dependent on distance of nucleus in question from the donor electron. This leads to various interesting features such as:

- The nuclear spin lattice relaxation rate is not the same for all nuclei, it has a distribution instead.
- Dynamic nuclear polarization of nuclei depends on the distance of that nuclei from the donor electron.
- The paramagnetic shift of nuclei also has a distribution.
- The tendency of a nucleus to relax via electrons depends on its distance from the electron and hence the leakage factor exhibits a distribution.
- As a result, the Overhauser shift is distance dependent and can therefore only be calculated by a numerical integration over the entire extension of the wavefunction.

As described in Chapter 2, the effective mass theory is an oversimplification. An amplification factor (referred to as core factor) needs to be included in the calculation of hyperfine interaction\(^{111,37}\) when using the hydrogen-like effective mass theory.

Equation 7.2 is thus modified as follows:

\[
A(r) = \left( \frac{8\pi}{3} \right) \cdot \left( \frac{\mu_0}{4\pi} \right) \cdot C g\mu_B \hbar \gamma_n |\psi(r)|^2
\]  

(7.3)

where \( C \) is the Core factor.

While the correct value of core factor is difficult to determine, an estimate for InP can be obtained by comparing the electron density in In atom\(^{80}\)

\[
|\psi|_{\text{atom}}^2 = 9.79 \times 10^{31} \text{ m}^{-3}
\]

to the average electron density in Indium metal (considering 1 valence electron per atom)

\[
|\psi|_{\text{metal}}^2 = 3.8 \times 10^{28} \text{ m}^{-3}
\]
Chapter 7: Modeling and Simulations

The core factor is thus given by:

\[ C = \frac{|\psi_{\text{atom}}|^2}{|\psi_{\text{metal}}|^2} \approx 2500 \]

This value can be used as a starting point in the simulation for Overhauser shift profiles and can be tuned to obtain perfect fitting between simulated and experimental data.

7.3 Nuclear Spin Lattice Relaxation Time

For nuclear relaxation via contact hyperfine interaction, the nuclear spin lattice relaxation time is given by:

\[ T_{1n}(r) = \frac{\hbar^2}{4\tau_c A^2(r)} \]

where \( \tau_c \) is the correlation time of fluctuation in HFI. We use the value of correlation time (=6ps) obtained from optically induced dynamic nuclear polarization measurements in InP \(^{112,113,114}\).

Using hyperfine interaction calculated in section 7.2 and correlation time =6ps, nuclear spin lattice relaxation rate can be calculated as a function of distance from the donor centre. This is shown in fig. 7.2. As can be clearly seen from this figure; the nuclei closest to the donor have the fastest relaxation rates. This is expected since these nuclei experience maximum hyperfine interaction. As the distance of the nuclei from the donor increases, the hyperfine interaction decreases and hence the nuclear spin lattice relaxation rate becomes slower. Fig. 7.2 shows that the nuclear spin lattice relaxation occurs via hyperfine interaction only within a distance of about 100 Å from the electron centre. For nuclei farther away, contribution from relaxation via hyperfine interaction is very small and can be safely neglected. These nuclei relax mainly via spin diffusion or quadrupolar relaxation.

An estimate for total nuclear spin lattice relaxation time can be obtained by summing over contributions from nuclei at various distances from electron centres as follows:

\[ T_{1bf} = \sum_{k=0}^{n (r_s=200\,\text{Å})} T_{1bf}(r_n)|\psi(r_n)|^2 \frac{4\pi r_n^2}{|\psi(r_n)|^2 4\pi r_n^2} \]
The above summation gives $T_{hf} = 73s$. This value is comparable to 105s (measured by Overhauser shift experiments) and much shorter than $T_1$ obtained from NMR (=526s). In NMR measurements (section 4.2), $T_1$ from bulk is measured. Nuclei in the bulk mainly relax via spin diffusion or quadrupolar relaxation. Both these processes are slower than the relaxation via scalar hyperfine interaction. The bulk measurement of $T_1$ thus gives a much longer time scale.

\[ \frac{1}{T_1e(s^{-1})} \]

Distance from donor (Å)

**Fig. 7.2: Nuclear spin lattice relaxation rate as a function of distance from the donor electron.**

### 7.4 Paramagnetic Shift

Another consequence of strong hyperfine interaction is the shift of nuclear resonance frequency due to the influence from the surrounding electrons. This shift is known as the Knight shift (due to conduction electrons in metals) or paramagnetic shift (due to paramagnetic centres or localized donor electrons) and is given by:

\[
K(r) = \frac{A(r)S_0(1-s_{ee})}{\gamma_n \hbar B_0} \times 10^5
\]

where $K$ is the paramagnetic shift (in ppm).
Fig. 7.3 shows the paramagnetic shift of $^{115}$In nuclei as a function of distance from the donor electron at 8K and for $s_{e\sigma r}=0.13$.

In InP, $^{115}$In nuclei and the electrons have the same sign of gyromagnetic ratio. Thus, the field from the electrons shifts the nuclear resonance position towards lower external field (lower frequency) resulting in negative paramagnetic shift (PM) shift. This is seen from the wings of the Overhauser signal profile at frequency lower than the resonance frequency. In silicon, the sign of shift is opposite and hence the wings of the Overhauser profile are on the opposite side. A comparison of fig. 7.3 and 5.18 shows that the width of the Overhauser line (on lower frequency side ~20 kHz) is consistent with the value of PM shift of nuclei in close proximity to the electrons obtained from the simulations.

**Fig. 7.3: Paramagnetic shift (in kHz) as a function of distance from the donor electron. $T=8K$, $s_{e\sigma r}=0.7$, $B_0=5589G$.**
7.5 Overhauser Shift

The nuclear field at the site of the donor electron due to a nucleus at distance \( r \) is given by:

\[
B_n(r) = \frac{A(r)\left(\frac{I_0}{I}\right)(1+V_{max} f_{esr})}{g \cdot \mu_B}
\]

Using hyperfine interaction \((A)\) obtained from the simulations, and values of \( f \) and \( s_{esr} \) obtained experimentally in chapter 5 \((f=0.147 \text{ and } s_{esr}=0.13)\), the nuclear field produced as a function of \( r \) is simulated and is shown in fig. 7.4.

![Nuclear Field vs Distance from Donor Electron](image)

*Fig. 7.4: Nuclear Field (in G) as a function of distance from the donor electron. T=8K, s_{esr}=0.13, f=0.143, C=2500, B_0=5589G.*
The total nuclear field at the electron position (i.e. the Overhauser shift) is obtained by a summation of contribution from all the nuclei.

\[ B_n = \sum_k B_n(r_k) \cdot N(r_k) \]

The contribution from nuclei at distance \( r \) \((B_n(r)N(r))\) to the total nuclear field is shown in fig. 7.5. It is seen that although the nuclear field falls off as the distance form the electron is increased, the maximum contribution to the Overhauser shift comes from \( r = 85\text{Å} \). Furthermore, since the contribution falls off rapidly for \( r > 85\text{Å} \) (8.5nm), it is justified to neglect the contribution of nuclei at \( r > 350 \text{ Å} \) (35nm). Thus, the total Overhauser shift due to \(^{115}\text{In} \) nuclei is given by:

\[ B_n = \sum_{k=0}^{n \left( r_k = 35 \text{nm} \right)} B_n(r_k) \cdot N(r_k) \]  (7.4)

The summation results for different simulation parameters are given in table 7.1. It is seen that core factor, \( C = 3200 \) gives a reasonable fit between measured and calculated Overhauser shifts.

---

**Fig. 7.5:** Contribution of nuclei to the total Overhauser shift (in G) as a function of distance from the donor electron. \( T = 8K, \) \( s_{esr} = 0.13, f = 0.143, B_0 = 5589 \text{ G} \)
Table 7.1: Different simulation parameters and the resulting $^{115}\text{In}$ Overhauser shift at 8K

<table>
<thead>
<tr>
<th>sesr</th>
<th>f</th>
<th>C</th>
<th>Ov. Shift (G) (simulation)</th>
<th>Ov. Shift (G) (measured)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.13</td>
<td>0.143</td>
<td>2500</td>
<td>38</td>
<td>50.6</td>
</tr>
<tr>
<td>0.13</td>
<td>0.143</td>
<td>3200</td>
<td>49</td>
<td>50.6</td>
</tr>
<tr>
<td>0.06</td>
<td>0.143</td>
<td>3200</td>
<td>23</td>
<td>23.5</td>
</tr>
</tbody>
</table>

7.6 RF Saturation Factor

The shift obtained from eqn. 7.4 is the total Overhauser shift created by all the nuclei at the electron position. The shift measured by double resonance technique, however, is not the complete shift and depends on the RF power used to depolarize the nuclei. Thus, an additional factor needs to be included in the simulated Overhauser shift as follows:

$$B_n(r) = \frac{A(r)\gamma B_0(1+V_{\text{max}}f_{\text{esr}})}{g\mu_B}, s_{RF}(r)$$

where $s_{RF}$ is the RF saturation factor and is given by:

$$s_{RF}(r) = \frac{(\gamma B_2)^2T_1(r)T_2}{1+(\gamma B_2)^2T_1(r)T_2}$$

Here $B_2$ is the RF field strength given by $B_2 = C_{\text{res}}\sqrt{P_{RF}}$, $T_1$ and $T_2$ are the nuclear spin lattice relaxation and nuclear spin-spin relaxation time respectively. We use the following values for these parameters:

- $T_1 = 200\mu$s (from spin echo measurement),
- $T_1 = 73s$ (from simulation)
- $C_{\text{res}} = 10.35\times10^{-6} T/\sqrt{W}$ (using Biot Savart law for the RF loop)

The RF power shown in fig 7.6 is the power applied from the RF synthesizer. However, not all of this power goes into the RF loop. We thus introduce a factor $Q$ such as: $B_2 = C_{\text{res}}\sqrt{OP_{RF}}$ where $P_{RF}$ is the power applied from the synthesizer. Different values of this parameter ($Q$) were tried in the simulations. It was observed that $Q=0.02$ gives a reasonable fitting of the experimental data. The simulated and the measured Overhauser shift as a function of $P_{RF}$ is shown in fig.7.6.
7.7 Conclusion and Outlook

It is seen that a simple model comprising of a homogenous distribution of donors in a semiconductor (wherein each electron localized at a donor centre interacts with the surrounding nuclei via contact hyperfine interaction) explains the experimental observations quite nicely. Simulations of various DNP related parameters (such as hyperfine interaction, nuclear spin lattice relaxation time, paramagnetic shift and Overhauser shift) using this model give values reasonably close to the measured ones. In order to improve the precision of simulations, other mechanisms operating in these semiconductors such as spin diffusion, overlap of electron wavefunction and subsequent electron hopping must be included in the model.
Chapter 8

Electric Current-Induced Dynamic Nuclear Polarization

After having laid down the basic principles of dynamic nuclear polarization and highlighting the importance of DNP processes in InP and GaAs, we now describe experiments to induce DNP in these semiconductors by means of electric current. InP and GaAs both have zinc-blende crystal structure and are thus expected to show CISP owing to the inversion asymmetry of the lattice. Our Overhauser shift measurements (Chapter 5) have shown clearly that huge DNP enhancement factors are possible in these wafers at low temperatures. Nuclear spin lattice relaxation measurements (Chapter 4) also prove the existence of strong hyperfine interaction needed for DNP processes. Furthermore, optical enhancement of nuclear polarization is well known in low doped InP\textsuperscript{112,115,116,117,118,119} as well as GaAs\textsuperscript{60,61,85} wafers. Both these semiconductors are therefore good candidates to study dynamic nuclear polarization induced by electric current.

Current induced DNP was investigated in InP by passing electric current through semiconductor wafers and measuring the nuclear polarization by means of standard NMR experiments. This is described in section 8.1. The effect of electric current on \textsuperscript{115}In and \textsuperscript{31}P nuclear polarization was
Chapter 8: Current-Induced Dynamic Nuclear Polarization

investigated on InP wafers with varying doping concentration. The critical doping concentration required for DNP build up is discussed. Section 8.2 describes measurements performed to study the time scale of build-up of DNP processes. In section 8.3 we discuss the temperature dependence of DNP. The observed recovery of the nuclear polarization after DNP is described in section 8.4. Current induced DNP experiments on GaAs are mentioned in section 8.5 and compared to similar measurements reported in the literature.

8.1 DNP Measurement

In order to investigate the effect of electric current on nuclear polarization, NMR experiments were performed while an electric field was applied across the semiconductor sample. For this purpose, a standard NMR probehead was modified to include electrical connections to a sample holder on which the sample is placed. In order to prevent current induced heating of the sample, the sample holder was provided with a sapphire on which the semiconductor sample was placed. This modified probehead and the sample holder are shown in fig. 8.1(a) and (b). Voltage applied to the sample was in the form of DC pulses instead of a continuous DC voltage. This facilitated control of heating by using suitable duty cycle of the pulsed voltage. Fig. 8.2 shows the geometry of the sample inside the NMR coil and inside the magnetic field. The nuclear spin polarization was measured with and without current pulses by means of pulse sequence shown in fig. 8.3 (a) and (b).

Fig. 8.1(a): NMR probehead with electrical connections to the semiconductor sample. (b): Sample holder with sapphire heat sink used for NMR measurements in presence of electric current.
Fig. 8.2 Orientation of the sample in the NMR coil with respect to magnetic field, $B_0$.

Fig. 8.3: Pulse sequences used to measure the effect of current on NMR signal intensity. (a): basic NMR measurement without DC pulses (reference measurement). (b): NMR measurement in presence of electric current.
NMR measurements under the effect of electric current were performed on metallic (sample #4) and undoped InP wafers (sample #6). No effect of current was observed on NMR measurements in metallic InP. Undoped InP (sample #6) showed a reduction in NMR signal intensity with increase in current strength. The reduction in NMR intensity due to current \( I_{dc} \) was measured for different current strengths and \( \eta \) vs. \( I_{dc} \) was recorded for various nuclei where \( \eta \) is defined as:

\[
\eta = \frac{\text{NMR signal intensity} \ (I_{dc} \neq 0)}{\text{NMR signal intensity} \ (I_{dc} = 0)}
\]

At this point, the difference between \( \eta \) and \( \phi \) must be noted. While \( \eta \) is the fractional decrease in NMR signal intensity on application of electric current, \( \phi \) denotes DNP enhancement of NMR signal intensity (as defined in eqn.2.20). The ratio \( \eta \) for \(^{115}\text{In}\) nuclei in undoped InP is plotted as a function of current in fig. 8.4. It is seen that at very low current strengths (<10mA), a small increase in NMR signal strength is observed. For higher current strengths, a reduction in the NMR signal intensity is observed.

Fig. 8.4: Fractional decreases in NMR signal intensity \( \eta \) for \(^{115}\text{In}\) as a function of current flowing through the semiconductor wafer (undoped InP, sample #6). Data points (●) are fitted by a stretched exponential function of the form

\[
y = A \exp\left(-\left(x/T_1^*\right)^\gamma\right).
\]
The observed reduction in NMR signal intensity could be due to heating produced by electric current. In order to check that possibility, the temperature of the InP sample in presence of electric current was monitored. For this purpose, a cernox temperature sensor was placed on the sample. It was observed that the electric current led to heating of the sample and a subsequent rise in sample temperature. Sample temperature was measured as a function of applied electric power at 8K and is shown in fig. 8.5.

\[
T = 8K + \beta \left( \frac{P_{\text{heating}}}{P_0} \right)^{0.8}
\]

where \( \beta = 0.287K \) and \( P_0 = 1 \text{mW} \). Sample temperature as a function of electric current is shown in the inset.

The sample temperature was monitored after the current pulses were switched off and it was observed that the temperature recovery happens within a few seconds. Temperature recovery to 8K after switching off the current pulses is shown in fig. 8.6. Therefore, in all the measurements involving current, the FID acquisition was performed after a delay of \( \sim 2 \text{sec} \) after switching off the current pulses. Although the FID measurement was done after the temperature recovery, the recovery of the spin polarization is much slower due to slow spin lattice relaxation.
rate. For example, the nuclear spin lattice relaxation time for $^{115}$In nuclei at 8K is \( \sim 800 \) sec. Hence, it takes several minutes for the nuclear spin polarization to recover to the value corresponding to 8K after the current pulses are switched off. Thus, we may conclude that the observed dependence of NMR signal intensity on electric current comes from two sources:

- Current induced dynamic nuclear polarization
- Reduction of NMR signal intensity due to heating

Fig. 8.6: Recovery of sample temperature to 8K (monitored by cernox sensor placed on the sample) after switching off the current pulses.

The respective contributions from the two above mentioned sources can be disentangled by calculating the expected reduction in NMR signal intensity due to heating using the Curie dependence. This is shown in fig. 8.7(a). After subtracting the heating effect from the measured NMR signal reduction, the net effect due to current induced dynamic nuclear polarization is separated. Two important observations from our data should be pointed out. First, the net nuclear polarization induced by electric current is positive. In other words, electric current induced dynamic nuclear polarization in InP has a positive sign resulting in enhancement of nuclear polarization. We measured a maximum enhancement of up to 50% which corresponds to enhancement factor,
\( \phi = 1.5 \). Secondly, this maximum DNP enhancement is obtained at a small current (10mA). With currents above this value, DNP enhancement starts to reduce. This could be attributed to a rise in temperature and hence lower DNP at higher current. As explained in chapter 4, \(^{115}\text{In} \) nuclei undergo quadrupolar relaxation at \( T > 15\text{K} \). Thus, an increase in temperature means a greater tendency to undergo quadrupolar relaxation and thus lower leakage factor. This results in lower dynamic nuclear polarization. The dependence of DNP on temperature is discussed in greater detail in section 8.3.

![Graph showing DNP enhancement and temperature effect against electric current](image)

**Fig. 8.7(a):** Reduction of \(^{115}\text{In} \) NMR signal intensity as a function of electric current measured in undoped InP at 8K. The contribution from temperature effect and the net dynamic nuclear polarization are shown separately.

A similar measurement for \(^{31}\text{P} \) in InP is shown in fig. 8.7(b). It was observed that \(^{31}\text{P} \) showed a much lower DNP enhancement as compared to \(^{115}\text{In} \). We have seen in \( T_1 \) measurements of \(^{115}\text{In} \) and \(^{31}\text{P} \) nuclei in undoped InP (chapter 4) that temperature dependence of \(^{31}\text{P} \) nuclear relaxation time follows \( T^{-0.4} \) trend as expected for relaxation via electrons in semiconductors. \(^{115}\text{In} \) nuclei however, show a tendency to undergo quadripolar relaxation. Thus, a higher DNP enhancement is expected for \(^{31}\text{P} \) as compared to \(^{115}\text{In} \). Furthermore, a higher DNP enhancement factor was obtained for \(^{31}\text{P} \) in Overhauser shift measurements as compared to
$^{115}\text{In}$ (chapter 5). Current-induced DNP measurements, on the other hand, show a lower enhancement for $^{31}\text{P}$ as compared to $^{115}\text{In}$. A likely reason for the discrepancy between expected and observed DNP enhancement is that $T_1$ of $^{31}\text{P}$ nuclei is longer than $^{115}\text{In}$ nuclei at 8K ($T_1(115\text{In})=527\text{s}$, $T_1(31\text{P})=1420\text{s}$). Therefore, current pulses need to be applied for a much longer duration in order to obtain complete DNP for $^{31}\text{P}$ nuclei. However, due to heating of the sample induced by dc current, the nuclear polarization is reduced before the complete buildup of DNP. Thus, the observed DNP enhancement is smaller for $^{31}\text{P}$ as compared to $^{115}\text{In}$ nuclei.

![Graph showing DNP enhancement vs. Temperature Effect and I(mA)](image)

**Fig. 8.7(b): Reduction of $^{31}\text{P}$ NMR signal intensity as a function of electric current measured in undoped InP at 8K. The contribution from the temperature effect and the net dynamic nuclear polarization are shown separately.**

### 8.1.1 Critical Doping Concentration for DNP

As mentioned earlier, similar measurements were performed on metallic InP (sample #4) as well. However, no effect of current was observed on NMR measurements in these samples.

From our resistivity measurements it was observed that the undoped InP (sample #6) shows a non-ohmic transport behavior. Metallic InP on the other hand, showed ohmic characteristics. The basic requirement for
building up current induced DNP in semiconductors is that electron system must be driven out of equilibrium. This is possible by application of an electric field which raises the electron kinetic temperature above that of the lattice. This requirement is met only in non metallic samples which show non linear transport effects.

The doping concentration of semiconductors also plays an important role in dynamic nuclear polarization processes. A detailed analysis of the dependence of electron spin relaxation on doping concentration in GaAs was done by Dzhioev et al.,\textsuperscript{120} The measured spin relaxation time and spin correlation time as a function of donor concentration are shown in fig. 8.8. At low donor concentrations, electrons are effectively isolated and their spins precess independently in random static nuclear fields. Thus, the electron-spin orientation is lost within a few nano-seconds. With increasing donor concentration, the electron wavefunction begins to overlap and the isotropic exchange interaction brings about flip-flop transitions. This results in dynamical averaging of the hyperfine interaction. The electron spin is no longer bound to a single donor and interacts with a greater number of nuclei, so that the effect of nuclear-spin fluctuations becomes smaller. As a result the spin relaxation time increases. Even stronger overlap of wavefunctions leads to a greater probability to lose spin orientation due to the anisotropic exchange interaction. Eventually, the anisotropic exchange interaction becomes stronger than the hyperfine interaction and the spin lifetime starts to decrease. The longest spin relaxation time occurs for doping concentration \( \approx 3 \times 10^{15} \text{cm}^{-3} \). Above the MIT, the Dyakonov-Perel mechanism of spin relaxation is dominant. The increase of electron concentration beyond MIT, leads to faster spin relaxation and thus shortening of spin relaxation time.

The exchange interaction at critical doping concentration \( \approx 3 \times 10^{15} \text{cm}^{-3} \) not only leads to long electron spin relaxation time, but also results in narrowing of the ESR line. Such exchange narrowed ESR lines have been observed in GaAs by J.S.Colton et al.,\textsuperscript{121} Samples with doping concentrations \( \approx 3 \times 10^{15} \text{cm}^{-3} \) display ESR linewidth close to 10 G which is the narrowest ever observed in GaAs. ESR lineshapes at different doping concentrations measured by the above mentioned authors are shown in fig.8.9. Such narrow lines in GaAs allow measurement of the Overhauser shift in these samples. Shifts of up to 60G have been reported\textsuperscript{121,122,123} in bulk GaAs with doping concentration \( \approx 3 \times 10^{15} \text{cm}^{-3} \).

It is evident from the above analysis that in bulk GaAs, electron spin relaxation time is longest when the doping concentration is lower than the MIT but is high enough to facilitate overlap of donor wavefunctions and hence isotropic exchange interaction. The exchange interactions
results in an exchange narrowed ESR line which appears to be an essential requirement for building up of dynamic nuclear polarization of Overhauser type.

Fig. 8.8: Spin relaxation time and spin correlation time as functions of donor concentration in n-GaAs. Figure reproduced from reference [120]
A similar investigation of dependence of dynamic nuclear polarization on donor concentration in InP was performed by Murakami et al. Overhauser shift of ESR line was measured by the authors in InP sample with doping concentration in the range $4.0 \times 10^{15} - 5.5 \times 10^{16}$ cm$^{-3}$. The results of measurements are shown in fig. 8.10. It was observed that the maximum Overhauser shift (and hence maximum DNP) occurs for donor concentration $\approx 9.0 \times 10^{15}$ cm$^{-3}$. Nuclear spin lattice relaxation rates were measured by following the recovery of ESR line position after switching off the microwave power. The dependence of the nuclear spin relaxation rate on donor concentration is shown in fig. 8.11. As is seen from the figure, the nuclear spin lattice relaxation time $T_{1N}$ decreases with increasing the donor concentration from $4.0 \times 10^{15} - 7.0 \times 10^{15}$ cm$^{-3}$ and then increases above $\approx 7.0 \times 10^{15}$ cm$^{-3}$.

Clearly, the peak of Overhauser shift and nuclear spin lattice relaxation time occur at a donor concentration $\approx 7.0 \times 10^{15}$ cm$^{-3} - 9.0 \times 10^{15}$ cm$^{-3}$. This appears to be the critical donor concentration which allows optimum overlap of donor wavefunctions resulting in maximum dynamic nuclear polarization. The undoped InP samples used in our measurements have a donor concentration ($\approx 7.0 \times 10^{15}$ cm$^{-3}$) which lies in this critical range. Metallic samples with doping concentration higher than the critical concentration are therefore not expected to DNP enhancements. This is consistent with our observations.
Fig. 8.10: Donor concentration dependence of Overhauser shift in InP measured at 4.2K. Figure reproduced from reference [78].

Fig. 8.11: Donor concentration dependence of nuclear spin lattice relaxation rate in InP measured at 4.2K. Figure reproduced from reference [78].
8.2 DNP Building Up

In order to investigate the time scale on which the observed current-induced DNP builds up, measurements were performed where the enhancement factors were measured for different DC periods (denoted by $\tau$) for a fixed current intensity. The dependence of enhancement factor on DC period is shown in fig. 8.12 for $^{115}$In at 8K for $I=30\, \text{mA}$. The $^{115}$In nuclear spin lattice relaxation time at this temperature is 526s. It was observed that for a fixed current intensity, the NMR signal strength reduces with the duration time of DC pulses ($\tau$). After subtracting the temperature effect from the measured data, the resultant net DNP effect was obtained as shown in fig. 8.12.

![Graph showing DNP enhancement as a function of DC pulses duration ($\tau$) for $I_{dc}=30\, \text{mA}$ at 8K.](image)

*Fig. 8.12: $^{115}$In DNP enhancement as a function of DC pulses duration ($\tau$) for $I_{dc}=30\, \text{mA}$ at 8K.*

The dynamic nuclear polarization is always expected to build up at a time scale equal to nuclear spin lattice relaxation time. In fig. 8.12, the net DNP effect is seen to increase with duration time of DC pulses ($\tau$) initially. However, as mentioned in the previous section, DC current pulses cause a temperature increase resulting in reduction of signal...
intensity. This is seen for $\tau > 1\text{sec}$. For building up of a complete DNP, the duration time of DC pulses should be at least $\sim 3T_1$ where $T_1$ is the nuclear spin lattice relaxation time. Due to heating of the sample, the nuclear spin polarization is reduced even before the complete build up of dynamic nuclear polarization occurs. Thus, one may conclude that the DNP enhancement factor for $^{115}\text{In}$ at 8K is certainly more than the observed value of 1.5.

### 8.3 Temperature Dependence of Current-Induced DNP

In order to investigate the temperature dependence of the current-induced dynamic nuclear polarization, measurements described in section 8.1 were performed on InP undoped sample at 25K. The observed reduction of the $^{115}\text{In}$ NMR signal intensity as a function of electric current at 25K is shown in fig. 8.13. Contributions from the temperature effect and the net dynamic nuclear polarization are shown separately. It is seen that the net DNP enhancement at 25K is much smaller than the corresponding value at 8K.

![Fig. 8.13: Reduction of $^{115}\text{In}$ NMR signal intensity as a function of electric current measured in undoped InP at 25K. The contribution from temperature effect and the net dynamic nuclear polarization are shown separately.](image)

---

Chapter 8: Current-Induced Dynamic Nuclear Polarization
The temperature dependence of current induced DNP is expected to come from the following factors:

- Temperature dependence of electron spin relaxation rate
- Temperature dependence of current induced electron spin polarization
- Temperature dependence of dynamic nuclear polarization

Each of these contributions will now be discussed separately.

Electron spin relaxation of conduction electrons in semiconductors occurs by the following three mechanisms:

- **D'yakonov and Perel mechanism:**
  In crystals that lack inversion symmetry, the spin-orbit interaction lifts the spin degeneracy: spin-up and spin-down electrons have different energies even when in the same momentum state. This is equivalent to having a momentum-dependent internal magnetic field $B(k)$ which is capable of flipping spins through the interaction term like $B(k)S$, with $S$ denoting the electron spin operator. This term can be further modulated by strain or by electric fields. D'yakonov and Perel’ showed that the lifting of the spin degeneracy leads to spin relaxation\(^\text{124}\). This type of spin relaxation is termed D'yakonov and Perel mechanism (DP mechanism). Investigations of the temperature dependence\(^\text{125}\) of DP spin relaxation in zinc-blende semiconductors have shown an increase in electron spin relaxation time by an order of magnitude on cooling from 300K to 4K.

- **Elliot Yafet mechanism:**
  The EY mechanism originates from the fact that, in the presence of spin-orbit coupling, the exact Bloch state is not a spin eigenstate but a superposition of them. This induces a finite probability for spin flip when the spatial part of electron wave function experiences a transition through scattering even if the involved interaction is spin independent. This was first observed by Elliot\(^\text{126}\). (Yafet\(^\text{127}\) showed that $1/T_1$ follows the temperature dependence of resistivity: $1/T_1 \sim T$ at temperatures $T$ above the Debye temperature, and $1/T_1 \sim T^5$ at very low $T$.

- **BIP mechanism:**
  Another source of spin relaxation for conduction electrons was found by Bir, Aronov, and Pikus\(^\text{128}\) in the electron-hole exchange interaction. This interaction depends on the spins of interacting electrons and holes and acts on electron spins as some effective magnetic field. The spin relaxation takes place as electron spins precess along this field.
In n-type zinc-blende semiconductors like GaAs and InP, DP and EY mechanisms of spin relaxation dominate. Since the efficiency of both these mechanisms has been shown to increase with temperature, electron spin relaxation time decreases with increase in temperature.

All experiments showing electrical generation of spin polarization in zinc-blende semiconductors reported in literature so far have been performed at cryogenic temperatures. The only semiconductor where electrical manipulation of spin polarization has been seen at room temperature is ZnSe. It appears that short spin coherence times of III-V semiconductors do not allow spin related effects to persist to higher temperatures.

As discussed in Chapter 5, the Overhauser enhancement factor depends on the gyromagnetic ratios of the electron and the nucleus and a “leakage” factor f. The leakage factor is 1 if nuclei relax only via the isotropic hyperfine interaction. Other mechanisms of nuclear relaxation lead to a short circuiting effect resulting in lower DNP. The leakage factor in such cases is defined by the ratio of relaxation rate via the contact hyperfine interaction ($\omega_c$) to the total relaxation rate ($1/T_1=\omega_c+\omega_i$) where $\omega_i$ is the relaxation rate due to processes other than the contact hyperfine interaction. Our measurements of the temperature dependence of nuclear spin lattice relaxation in undoped InP (and GaAs) showed that quadrupolar relaxation is the preferred mode of nuclear relaxation at T>15K. Only at T<15K, $^{115}$In nuclei tend to relax via electrons. Thus, DNP is expected to become much less efficient at T>15K. This is confirmed by comparison of InP Overhauser measurements at 8K with literature values at 4.2K. B. Gotschy et al. measured InP samples with similar doping concentration at 4.2K and obtained DNP enhancement factors almost twice the values reported in this dissertation (at 8K). Furthermore, several optical NMR measurements in InP and GaAs also confirm that dynamic nuclear polarization via contact hyperfine interaction is most efficient at low temperature.

A consequence of the above mentioned factors is that current induced DNP is highly temperature dependent. This explains much lower DNP enhancement observed at 25K as compared to 8K. Reduction in DNP at high temperature also explains the lower DNP enhancement factors measured at I>10mA (fig. 8.6).
8.4 Nuclear Magnetization Recovery

The pulse sequence used to monitor the recovery of nuclear polarization after DC current pulses are switched off is shown in fig. 8.14. It was observed that when current pulses are switched off after reduction of nuclear polarization, the recovery of nuclear polarization to its original state (corresponding to $\eta = 1$) follows a trend: $(1 - \exp(-t/T_1))$ where $T_1$ is the nuclear spin lattice relaxation time at that temperature. This is shown in fig. 8.15 for $^{115}$In nuclei in InP at 8K.

![Pulse sequence](image1)

**Fig. 8.14:** Pulse sequence used to monitor the recovery of nuclear polarization after the DC pulses are switched off.

![Graph](image2)

**Fig. 8.15:** Recovery of nuclear polarization at 25K after the DC pulses are switched off. Fitting function is of the form: $y = A_0(1 - \exp(-\tau / T_1)) + B$ where $T_1 = 528s$. The nuclear spin lattice relaxation time for $^{115}$In at 8K is 526s.
As discussed in section 8.1, the decrease of nuclear polarization on application of electric current includes two independent contributions: (i) heating and (ii) DNP effects. Thus, the recovery of nuclear polarization to equilibrium value (corresponding to $\eta=1$) involves recovery of part of nuclear polarization which was destroyed by heating as well as the recovery of part of nuclear polarization enhanced via DNP processes. Nuclear polarization diminished by heating recovers to the polarization corresponding to 8K at a time scale equal to nuclear spin lattice relaxation time at 8K. Also, the nuclear polarization enhanced by means of DNP processes recovers with the same time scale. Thus, both the recoveries are expected to happen at nuclear $T_1$ time at 8K. This is consistent with our observations.

### 8.5 Current Induced DNP in Low Doped GaAs

Measurements described above for InP were performed on just metallic GaAs samples (sample#2 and #3). These samples are similar to the ones measured by Hoch et al.\textsuperscript{130} for investigation of current-induced DNP in GaAs. Negative DNP effects have been reported by the authors in low doped GaAs samples of doping concentration $1.55 \times 10^{15}$ cm$^{-3}$. Our measurements on GaAs showed a reduction in nuclear polarization similar to InP but no net DNP was observed. Relative decrease of NMR signal for sample#2 as a function of electric current is shown in fig.8.16. Temperature effect and DNP effect are shown separately in fig. 8.17. As is clear form this figure, no conclusive DNP effects were observed. A likely reason for lack of DNP effects is that the doping concentration of samples used in reference [130] is $5.9 \times 10^{15}$ cm$^{-3}$ whereas our samples have a doping concentration equal to $2.5 \times 10^{16}$ cm$^{-3}$. As discussed in section 8.1, critical doping concentration for DNP in GaAs appears to be close to $\approx 3.0 \times 10^{15}$ cm$^{-3}$. Since doping in our sample #2 is much higher than the apparent critical doping concentration, DNP build up may not occur in this sample. Sample #3 ($n=1.2 \times 10^{15}$ cm$^{-3}$) on the other hand has concentration lower than the critical concentration. For such low doping concentration, carrier freeze out starts to occur at 150K and hence current induced DNP measurements are not possible at lower temperature.
Chapter 8: Current-Induced Dynamic Nuclear Polarization

Fig. 8.16: Fractional decrease in $^{71}$Ga nuclear polarization ($\eta$) as a function of current flowing through GaAs ($2.5 \times 10^{16}$ cm$^{-3}$) at 8K.

Fig. 8.17: Reduction of $^{71}$Ga NMR signal intensity as a function of electric current measured in GaAs ($2.5 \times 10^{16}$ cm$^{-3}$) at 8K. The contribution from temperature effect and the net dynamic nuclear polarization are shown separately.
Chapter 8: Current-Induced Dynamic Nuclear Polarization

8.6 Discussion and Conclusion

We now briefly compare the DNP mechanism induced by microwave saturation (described in Chapter 5 and 6) with current-induced DNP. The equation for dipolar or scalar relaxation of the first kind can be written as\(^7\):

\[
\frac{d\langle I_z \rangle}{dt} = \frac{-1}{T_{rel}} \left[ \langle I_z \rangle - I_0 + \xi \frac{I(I+1)}{S(S+1)} \langle S_z \rangle - S_0 \right] \tag{8.1}
\]

Here, \(T_{rel}\) is the electron nuclear relaxation time, \(\xi = -1\) for scalar relaxation and \(\xi = 1/2\) for dipolar relaxation. In the long-time scalar limit, taking \(d\langle I_z \rangle/ dt = 0\) gives:

\[
\left[ \langle I_z \rangle - I_0 = \frac{I(I+1)}{S(S+1)} \langle S_z \rangle - S_0 \right] \tag{8.2}
\]

The equilibrium values \(I_0\) and \(S_0\) are given by:

\[
\langle S_0 \rangle = \frac{-g^* \mu_b S(S+1)B_0}{3kT} \quad \text{and} \quad \langle I_0 \rangle = \frac{\gamma_n h(1+1)B_0}{3kT}
\]

Using these in eqn. 8.2 gives the following expression for DNP enhancement factor:

\[
\phi = \frac{\langle I_z \rangle}{\langle I_0 \rangle} = 1 - \frac{g^* \mu_b \langle S_z \rangle - S_0}{\gamma_n h S_0} \tag{8.3}
\]

Thus, for \(\langle S_z \rangle < \langle S_0 \rangle\),

- \(\phi\) is expected to be positive for InP \((g^* = 1.26)\)
- \(\phi\) is expected to be negative for GaAs \((g^* = -0.44)\)

This confirms with the observation of nuclear enhancement seen in our measurements on InP and of negative DNP observed by Hoch et al. \(^{130}\) in GaAs.

Expression (8.3) is similar to the Overhauser enhancement factor for microwave induced dynamic nuclear polarization (refer to Chapter 5). Microwave-induced DNP and current-induced DNP essentially are based on the same working principle. The only difference between the two
techniques is the method of driving electron spin polarization out of equilibrium. In standard Overhauser technique, microwaves are used to drive the electron spin system out of equilibrium. In current induced DNP, electric current and the subsequent spin-orbit coupling effects result in non equilibrium electron spin system. Mechanism of current induced electron spin polarization in zinc-blende semiconductors has been already discussed in detail in chapter 2.

The fact that the electric field drives electron spin polarization (and hence electron spin temperature) out of equilibrium has been experimentally observed in zinc-blende semiconductors. In the presence of a large electric field that induces nonlinear transport effects, it is well established that in GaAs\textsuperscript{131,132,133} and InP\textsuperscript{134} the electron kinetic temperature ($T_R$) rises above that of the lattice ($T_L$) i.e. $T_R > T_L$. Theoretical predictions\textsuperscript{135} of spin relaxation time in GaAs ($n = 10^{16} \text{cm}^{-3}$) at 5K give $\tau_s = 6000\text{ns}$. Experimentally\textsuperscript{136}, however, much shorter relaxation time (100ns) has been measured. Spin temperature ($T_S$) rising through spin orbit coupling effects to the hot electron temperature in a time $\sim \tau_s$ (thus resulting in $T_S = T_R$) explains these shorter than predicted spin relaxation times. DNP is therefore driven by the difference between $T_S$ and $T_L$.

Expressing $\langle S_x \rangle$ and $\langle S_y \rangle$ in terms of electron spin temperature ($T_S$) and lattice temperature ($T_L$), eqn. (8.3) becomes:

$$\phi = \frac{\langle I_x \rangle}{\langle I_0 \rangle} = 1 - \frac{g^* \mu_B}{\gamma_i \hbar} \left( \frac{T_L - T_S}{T_S} \right)$$

(8.4)

$T_S > T_L$ therefore leads to positive sign of DNP enhancement in InP and negative sign of DNP enhancement in GaAs.

If hyperfine coupling between itinerant electrons and nuclei is sufficiently large, the above mentioned mechanism of DNP occurs directly through conduction electrons. However, as was observed experimentally from Overhauser measurements (Chapter 5 and 6) and simulations (Chapter 7), for low doped InP and GaAs, hyperfine coupling of the nuclei with localized electrons is much stronger than the coupling with conduction electrons. In such a scenario, the role of localized intermediaries cannot be ruled out. Since it is known that the itinerant and localized electron spins reach thermal equilibrium through rapid exchange processes in a short time ($\sim 10\text{ps}$)\textsuperscript{31}, one may assume that the complete electron spin system (itinerant and localized electrons) can be described by a single temperature ($T_S$). This spin temperature when driven out of equilibrium
with respect to the lattice temperature ($T_L$) results in dynamic nuclear polarization.

We thus conclude that InP wafers with doping concentration $6.7 \times 10^{15} - 8 \times 10^{15}$ cm$^{-3}$ exhibit strong Overhauser type dynamic nuclear polarization at $T < 20$K. The electron spin system can be driven out of equilibrium by means of electric current consistent with model predictions and experimental studies in zinc-blende semiconductors. The maximum DNP enhancement factor measured in these samples was 1.5. Much higher enhancement is expected if heating due to current can be avoided. In contrast to these effects seen in low doped InP, no effect of current was observed in metallic and insulating InP and GaAs.

### 8.7 Outlook

More precise and conclusive measurements can be performed on low doped InP if heating effects can be avoided. Our 4-point resistivity measurements on these wafers have shown that the metal–semiconductor contact resistance is much higher than the intrinsic resistance of the semiconductor sample. This leads to localized heating at the contacts resulting in lower DNP enhancement. Better electrical contacts must be tried in order to alleviate current-induced heating effects.

Once the heating effects are avoided, measurements can be performed to investigate the time scale of DNP build-up processes as well as the effect of electric current on nuclear spin lattice relaxation rates. These measurements are likely to elucidate the role of itinerant and localized electron in the DNP mechanism. Furthermore, reduction of heating effects will enable measurement of current-induced DNP enhancement in $^{31}$P nuclei as well. Due to stronger hyperfine interaction and higher leakage factor (no quadrupolar relaxation), $^{31}$P is expected to show much higher DNP enhancement as compared to $^{115}$In.
Chapter 9

Spin Gunn Effect

9.1 Gunn Effect

The Gunn effect, discovered by J.B.Gunn in 1963, is caused by peculiarities in the conduction band structure of some direct band gap semiconductors such as GaAs and InP. Fig.9.1 shows the energy momentum diagrams for GaAs and InP. These two are the most preferred semiconductors for Gunn devices and have very similar band structures. The bottom of the conduction band is located at $k=0$ (Γ point). The first higher subband is located along the $<111>$ axis (L point). The Γ point and the L point (i.e. the lower valley and the upper valley) have an energy separation of 0.31eV for GaAs and 0.53eV for InP. The effective mass, mobility and the electron density in lower and upper valleys are denoted by ($m_1^*$, $\mu_1$, $n_1$) and ($m_2^*$, $\mu_2$, $n_2$) respectively. In case of GaAs the mobility and effective mass in lower and upper valleys are given by:

<table>
<thead>
<tr>
<th>Valley</th>
<th>Lower Valley</th>
<th>Upper Valley</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mobility(cm$^2$/Vs)</td>
<td>8000</td>
<td>180</td>
</tr>
<tr>
<td>Effective mass(m$_0$)</td>
<td>0.068</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Table. 9.1: Mobility and effective mass in GaAs
In equilibrium at room temperature, most electrons reside near the bottom of the lower $\Gamma$ valley. At small electric fields, the electric current increases linearly with electric field and the device acts as a passive resistance device. However, since the mobility is high in the lower valley, at high enough electric field ($E_{\text{th}}$), they can readily be accelerated to energies of the order of $\Gamma$-$L$ intervalley separation. Electrons are thus scattered into the $L$ valley resulting in a decrease in average electron mobility.

This decrease of electron velocity (current) with increase in electric field beyond the threshold voltage gives rise to negative differential resistance (NDR). This is the essential feature responsible for current instabilities and Gunn oscillations. A typical I-V curve and the NDR for a GaAs Gunn diode are shown in fig. 9.2.
Consider a sample of uniformly doped n-type GaAs of length L biased with a constant voltage source $V_0 (>V_{th})$. The electric field is thus given by $E_0 = \frac{V_0}{L}$. The electrons flow from cathode to anode with a constant velocity $V_3$. (fig. 9.3(c)). Consider, a small local perturbation in the charge arising at $t=t_0$, (fig. 9.3(a)). The resulting electric field distribution is shown in fig. 9.3(b). The electrons at point A experience an electric field $E_{L1}$ and travel to the anode with velocity $V_4$. The electrons at point B are subjected to an electric field $E_{H1}$ and hence have velocity $V_2$ which is smaller than $V_4$. Consequently, a pile-up of electrons occurs between A and B, increasing the net negative charge in that region. The region immediately to the right of B thus becomes progressively more depleted of electrons due to their higher drift velocity towards the anode than those at B. As a result, the initial small perturbation gradually grows into a dipole domain (known as a Gunn domain). These Gunn domains grow while propagating towards the anode until a stable domain has been formed. One such domain is shown in fig. 9.3 (a). In a stable domain, the electrons at points C and D move at same velocity $V_1$. Successive formation and drift of these Gunn domains through the sample leads to ac current oscillations observed at the contacts.
Fig. 9.3 Profile of (a) charge density, (b) electric field and (c) electron drift velocity in a biased sample of length $L$. 
9.2 The Spin Gunn Effect

As seen in section 9.1, the difference in electron mobility in the two valleys drives the standard Gunn effect. The electron mobility is however spin dependent in many semiconductors. Thus, a small spin polarization (created either by a random thermal fluctuation or spin-orbit effects) is expected to grow and lead to spin polarized domains. This is termed as the "Spin Gunn Effect" A theoretical calculation and prediction of this effect resulting in the generation of spin polarized current pulses in GaAs and InP was published recently by Qi et al and will be outlined briefly in this section.

The predicted spin Gunn effect is based on the dependence of the electron drift velocity on spin polarization. The electron mobility depends on the carrier density and thus the mobility for spin up and spin down carriers differs in most semiconductors. This is shown in fig. 9.4. Due to the Pauli exclusion principle, the chemical potentials of spin-up and spin-down electrons in a spin polarized electron gas are different. Thus, in a polarized degenerate electron gas, the energy distributions of spin-up and spin-down electrons differ. Furthermore, the mobilities for \( P \neq 0 \) will differ from \( P = 0 \). The difference in mobilities of spin-up and spin-down electrons can be estimated by defining a parameter \( \beta \) as:

\[
\beta = \lim_{P \to 0} \frac{\mu_u - \mu_d}{2P \mu_{av}}
\]

(9.1)

where \( \mu_u = \mu(n_u) \) and \( \mu_d = \mu(n_d) \) is the mobility for spin up and spin down carriers respectively and \( \mu_{av} = (n_u \mu_u + n_d \mu_d) / (n_u + n_d) \)

For scattering of conduction electrons from ionized impurities, acoustic phonons via piezoelectric coupling, or longitudinal phonons via Fröhlich coupling (LO phonon scattering), the low-energy electrons are scattered more than the high-energy electrons. In a spin polarized electron gas, the higher energy of spin-up electrons results in longer scattering times (and thus a higher mobility) than the spin-down electrons. This situation corresponds to \( \beta > 0 \). If the dominant scattering process involves acoustic phonon coupling via the deformation potential (DP-phonon scattering), then the spin-up electrons have lower mobility than the spin-down electrons resulting in \( \beta < 0 \). Thus, for \( P \neq 0 \), even when there is no direct spin dependence of scattering processes, the mobility of electrons is almost always strongly dependent on spin orientation. Thus, \( \beta \neq 0 \) when \( P \neq 0 \) resulting in amplification and growth of spin Gunn domains until they reach a saturation limit. Results of calculations for GaAs and InP for \( \beta \) performed in reference [140] are shown in fig. 9.5.
Eq. 9.4: Scattering of spin-up and spin-down electrons.[Fig. from reference 140]

(a) Electrons are unpolarized and the mobility of spin-up and spin-down electrons is identical.
(b) Electrons are polarized and the mobility of spin-up and electrons is either smaller ($\beta<0$, purple curve) or larger ($\beta>0$, green curve) than the mobility of spin-down electrons.

It has been shown by Qi et al\textsuperscript{140} that the time dependence of spin polarization of electrons ($P$) in an initially unpolarized charge Gunn domain may be described by the equation:

$$\frac{\partial P}{\partial t} \sim \left( \gamma - \frac{1}{T_i} \right)^P$$

where factor $\gamma$ depends on $\beta$ as well as on the mobility, electric field, electron density and velocity within a charge Gunn domain. This equation predicts spin amplification if $\gamma > T_i^{-1}$ resulting in a growth of spin polarization until it reaches a saturation limit. Fig. 9.6 shows the calculated position dependence of electron density, the electric field, spin amplification rates and saturation spin polarization within a domain. As is clear from the figure, the predicted spin Gunn effect results in a pulse of highly spin-polarized electrons located just before of just after a charge current pulse. As per the calculations in the reference, the spin polarized domains may have saturation polarization as large as 80% in GaAs and InP.
Fig. 9.5: (a), (b): $\beta$ as a function of electron concentration for GaAs and InP at 300K (dashed line) and 500K (solid line). [Fig. from reference 140] (c), (d) $\beta$ as a function of temperature for GaAs and InP for $n=10^{18}\text{cm}^{-3}$. Green curves are LO-phonon scattering, blue curves are ionized impurity scattering, red curves are piezoelectric-phonon scattering, and black curves are DP-phonon scattering.

**Spin Gunn Effect: Detection via Dynamic Nuclear Polarization**

As seen from fig. 9.6, within the spin Gunn regime, spin polarized domains extending in space to a few $\mu$m are formed in InP and GaAs. Within such a spin Gunn domain, electron spin polarization of up to unity may be achieved. Since, the electron system is driven out of equilibrium; it has a tendency to relax to the equilibrium. We have already shown in previous chapters that both InP and GaAs exhibit strong hyperfine coupling and huge DNP enhancement factors may be reached under suitable conditions. Thus, within a spin Gunn domain, the transitions of electron spin system towards thermal equilibrium are expected to dynamically polarize nuclear spins. As was discussed in chapter 8, localized paramagnetic intermediaries may also play a role in polarization transfer mechanism from conduction electrons to the lattice.
nuclei. We thus propose a method of detection of spin Gunn domains by measuring their effect on nuclear polarization. For this purpose, we performed standard NMR measurements on InP and GaAs wafers with varying doping concentration in the presence of electric field. Different types of samples used and other experimental details of the measurements are described in the next section.

---

**Fig. 9.6:** Position dependence of the density $n$ (a and b) and the electric field $E$ (c and d) in the domain frame. Spin amplification rate for DP-phonon scattering (e and f) and LO-phonon scattering (g and h). The three curves correspond to different drift velocities far from the domain. Black is $5.7 \times 10^6$ cm/s for GaAs, $2.6 \times 10^7$ cm/s for InP. Red is $5.0 \times 10^6$ cm/s for GaAs, $2.45 \times 10^7$ cm/s for InP. Blue is $4 \times 10^6$ cm/s for GaAs, $2.4 \times 10^7$ cm/s for InP. Saturation spin polarization (i and j) [Fig. from reference 140]
9.3 Experimental Details

Since the calculations described in reference [140] predict that the parameter $\beta$ is expected to increase with increase in electron concentration, our first choice for the investigation of this effect was metallic GaAs ($n = 2.1 \times 10^{19}$ cm$^{-3}$). Electrical contacts were made on the samples as described in section 4.1. The sample holder used for the measurements had a sapphire substrate which acts as a heat sink to prevent ohmic heating of samples. Commercially available metallic GaAs wafers were polished to 100 $\mu$m thickness in order to avoid very high Gunn threshold voltage. The Gunn threshold field for GaAs is 0.32V/$\mu$m. Thus, a 100$\mu$m thick wafer is expected to show negative differential resistance at 32V. Fig. 9.7 shows an IV curve for metallic GaAs sample of dimension $4 \times 2 \times 0.1$ mm$^3$. The I-V curve is non-linear at low voltages due to non-ohmic behaviour of the electrical contacts. Since the resistivity of such a wafer is very small, huge currents flow even at voltages much lower than the Gunn threshold voltage resulting in heating of the samples. Severe heating effects leading to the destruction of contacts and/or the semiconductor wafer were observed. In order to avoid the heating effects, smaller dimensions of the sample were used ($1 \times 1 \times 0.1$ mm$^3$). It is to be noted that since NMR signal intensity reduces with a decrease in sample volume, further reduction in wafer dimensions did not allow us to measure NMR signal with decent signal/noise ratio. Further efforts to reduce heating effects included:

- using DC voltage in the form of pulses with very short duty cycle, and
- increasing the area of the metal-semiconductor contacts.

However, even after all these improvements; the maximum voltage that could be applied without destroying the wafers was $\sim$10V. This is far below the Gunn threshold needed for bulk GaAs. Within the reachable voltage range, NMR measurements were performed with and without an applied electric field. However, no effect of the applied voltage on NMR signal intensity was observed.

Similar measurements were performed on metallic InP ($n = 7 \times 10^{19}$ cm$^{-3}$) wafers of dimension $1 \times 1 \times 0.1$ mm$^3$. Due to high conductivity of metallic InP, heating problems similar to GaAs were encountered in this sample as well. Furthermore, Gunn threshold for InP (10.5kV/cm) is much higher than GaAs (3.2kV/cm). Therefore, reaching Gunn regime in InP is harder than in GaAs. Within the reachable voltage range, no effect of electric field was observed on NMR signal intensity in this sample.
Fig. 9.7: I-V curve for metallic GaAs \((n=2.1 \times 10^{19} \text{ cm}^{-3})\) sample of dimensions \(4 \times 2 \times 0.1 \text{ mm}^3\) at 300K.

Fig. 9.8: I-V curve for SI-GaAs sample of dimensions \(4 \times 2 \times 0.5 \text{ mm}^3\) at 300K.
Due to high conductivity of metallic GaAs and InP, it was impossible to reach respective Gunn threshold voltages in bulk samples of these semiconductors. Thus, Semi-Insulating GaAs (SI-GaAs) bulk wafers of dimension $4 \times 2 \times 0.5 \text{ mm}^3$ were tried next. The electron concentration in such a sample is $n \sim 10^{14}\text{cm}^{-3}$ and NDR is expected to set in at 160V. A typical I-V curve for this sample is shown in fig. 9.8. Though no clear Gunn oscillations were observed, current instabilities at voltages higher than 175V were observed. Basic NMR experiments were performed in presence of DC voltage applied across the sample thickness. The dependence of NMR signal intensity on applied voltage is shown in fig. 9.9. As seen from the figure, about 15% reduction in NMR signal intensity was observed on application of DC voltage as high as 200V. The observed reduction in signal intensity is gradual and no abrupt changes are seen above and below the expected Gunn threshold (160V). If DNP induced by the spin Gunn effect operates in this sample, an abrupt change in NMR signal intensity is expected when the voltage is increased beyond the Gunn threshold. The observed gradual effect therefore does not look like the spin Gunn effect. Moreover, since the current flowing through the SI sample is very small, heating induced by the DC voltage can be safely neglected. Therefore, we attribute the observed reduction in signal strength to current-induced DNP related effects as discussed in chapter 8. Since the electronic g-factor is negative in GaAs, negative DNP resulting in a decrease in NMR signal intensity is expected if current-induced DNP operates. Furthermore, SI GaAs grown by liquid encapsulated Czochralski (LEC) is known to have EL2 defects. These are electron traps below the conduction band usually attributed to an As$_{Ga}$ antisite defect. The singly ionised charged state of this defect EL2$^+$ is paramagnetic and thus may play a crucial role in hyperfine mediated dynamic nuclear polarization mechanism.

Nuclear spin lattice relaxation rates for $^{75}$As were measured in presence of applied electric field. However, due to rather small effects (15%), no clear dependence of nuclear $T_1$ time on applied electric field was observed.

As has been discussed in detail in earlier chapters, DNP effects in III-V semiconductors become more pronounced at low temperatures. Therefore, in order to enhance the DNP effects, SI GaAs samples were cooled below room temperature. Fig. 9.10 shows I-V curves for SI-GaAs sample of dimension $4 \times 2 \times 0.5 \text{ mm}^3$ at different temperatures. It is seen that below 250K, the current intensity reduces below the measurable range of 1nA. Therefore, the effect of electric field on nuclear polarization could not be investigated in this sample at temperatures lower than the room temperature.
Fig. 9.9(a): $^{75}$As NMR signal intensity with and without the applied DC voltage at 300K.

Fig. 9.9(b): $^{75}$As NMR signal intensity as a function of applied DC voltage at 300K. Dotted line is a guide to the eye.
Fig. 9.10: Log-log plot of current (I) vs. applied voltage (V) for SI-GaAs sample of dimensions 4×2×0.5 mm³ at different temperatures.

Since it was not possible to reach the respective Gunn threshold voltages in bulk wafers of metallic as well as semi-insulating GaAs and InP samples, our next choice of sample for investigating possible spin Gunn effect was thin wafers of low doped GaAs. Standard Gunn devices made of GaAs have doping levels in the range of 10¹⁴-10¹⁶ cm⁻³. GaAs layers of thickness 5μm with doping concentration n=1×10¹⁶ cm⁻³ were grown on metallic GaAs substrate by Molecular Beam Epitaxy (MBE). Various layers in the structure are shown in fig. 9.11(a). A typical IV curve for such a sample of dimension 4×2×0.2 mm³ is shown in fig. 9.11(b). The Gunn threshold for this sample is 1.6V. However, these samples did not show negative differential resistance for voltages as high as 3.5V. This discrepancy could be caused by high resistivity of Au-Ge electrical contacts. It is evident from fig. 9.11(b), the metal-semiconductor contacts made from Au-Ge are non-ohmic; resulting in a potential drop across the contacts. Thus, the actual field across the active layer may not have reached the Gunn threshold (1.6V). A much higher voltage needs to be applied across this sample in order to reach the Gunn threshold. However, high current intensity led to localized heating at the contacts resulting in destruction of the contacts and/or sample beyond 3.5V. In order to avoid heating effects, the area of the sample must be reduced. Moreover, better electrical contacts are also essential for avoiding any
potential drop across the contacts. For this purpose, commercial GaAs Gunn diodes (in die form) were used for investigation of spin Gunn effect. The GaAs Gunn diodes with electrical contacts made of Au fabricated on both the surfaces by evaporation and annealing processes were obtained from Microwave Technology (MwT). The specifications of the diodes are given in table 9.2.

![Gunn structure diagram](image)

**Fig. 9.11:** (a) Gunn structure fabricated by growing a low doped GaAs layer on n-GaAs substrate. (b) Typical I-V curve of such a structure of area 4×2mm² at 300K. Duty cycle used for the measurement:1%.
Table 9.2: Specifications of Gunn diodes used for measurements.

<table>
<thead>
<tr>
<th>Name</th>
<th>MwT-GK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency Range</td>
<td>K-Band (18 to 26.5GHz)</td>
</tr>
<tr>
<td>Dimensions</td>
<td>250×250×80μm³</td>
</tr>
<tr>
<td>Output Power</td>
<td>11to13dBm</td>
</tr>
<tr>
<td>Threshold Voltage</td>
<td>6V</td>
</tr>
<tr>
<td>DC Current</td>
<td>140to 220mA</td>
</tr>
<tr>
<td>Maximum Bias Voltage</td>
<td>7.5V</td>
</tr>
<tr>
<td>Storage temperature</td>
<td>-55 to +120C</td>
</tr>
</tbody>
</table>

The I-V curve was measured for these diodes and is shown in fig 9.12. It is to be noted that due to better metal-semiconductor contacts, these diodes show almost perfect ohmic behaviour at low voltages. The NDR region above 6V is clearly evident. Gunn oscillations were observed in current pulses at V>5.5V. This is shown in fig 9.13.

Fig. 9.12: I-V curve for GaAs Gunn diodes measured at 300K, Pulse width= 4μs and Duty cycle=4%.
Due to small volume of the samples \((5 \times 10^{-3} \text{mm}^3)\), it was not possible to obtain a measurable NMR signal from a single diode. Thus, multiple Gunn diodes were stacked on a sample holder to increase the sample volume. However, even with 6 Gunn diodes no NMR signal could be detected at room temperature. At low temperatures, the nuclear \(T_1\) times in GaAs are rather long (about 100s at 30K). Therefore, standard NMR pulse sequence \((\pi/2\) pulse followed by FID acquisition and delay \((\sim 5T_1)\) after each acquisition\) was not well suited for measurement at low temperatures. A pulse sequence similar to FLASH (Fast Low Angle Shots) was used for measurements at low temperature. Fast, repetitive scans using very short radio frequency pulses were used to accumulate signal for a long duration of time. Using RF pulses much shorter than the \(\pi/2\) pulse length enables fast measurement by avoiding long delay times needed at low temperatures due to long \(T_1\) times. Fig. 9.14 (a) shows the acquired FID (after Fourier transform) using standard NMR pulse sequence. No clear NMR signal was detected after 12min of measurement time. On the other hand, a good NMR signal \((S/N \sim 4)\) could be seen after the same measurement time using FLASH-like pulse sequence. This is shown in fig. 9.14(b).
Fig. 9.14: $^{75}\text{As}$ NMR signal measurement at 30K (a) using standard NMR pulse sequence and (b) using fast low angle shots.
In order to investigate the effect of Gunn oscillations on the nuclear polarization in the Gunn diode sample, one of the 6 diodes was electrically connected for application of voltage pulses. NMR measurements were performed after application of DC voltage pulses. The pulse sequences used for this purpose are shown in fig.9.15. The first sequence is used for a reference measurement where DC pulses with voltage less than the Gunn threshold voltage for the GaAs Gunn diodes are applied. In the second sequence, DC voltage pulses exceed the Gunn threshold and thus Gunn oscillations are observed. NMR signal intensity within the Gunn regime is compared with the reference NMR signal intensity.

Fig. 9.15: Pulse sequences used to measure the effect of Gunn oscillations on NMR signal intensity. (a): basic NMR measurement with DC pulses of voltage less than the Gunn threshold (reference measurement). (b): NMR measurement in presence of Gunn oscillations.

Fig.9.16 shows one such comparison of $^{75}$As NMR signal intensity within and outside the Gunn regime at 50K. The duty cycle used for this measurement is 10%. No conspicuous difference between the two NMR signals was observed. In order to improve the signal/noise ratio, temperature was further reduced. However, with decrease of temperature
the Gunn threshold voltage increases. The Gunn threshold voltage is shown as a function of temperature in fig. 9.17. Higher threshold voltage leads to higher ohmic heating of the sample. The increase of duty cycle of DC pulses also leads to increased heating. At high duty cycles and low temperatures, ohmic heating at the electrical contacts led to breaking of sample contacts. NMR measurements at 10K and 4% duty cycle are shown in fig. 9.18. No discernable change in the NMR signal intensity is seen for these settings as well. The maximum duty cycle that could be used for the measurements was 40% (at 75K). No effect of Gunn oscillations was seen on the NMR signal intensity even with 40% duty cycle.

![Graph showing NMR signal intensity at 50K with RF frequency on the x-axis and signal intensity on the y-axis. Two lines represent V<V<sub>th</sub> and V>V<sub>th</sub>.](image)

*Fig. 9.16: 75As NMR signal intensity at 50K. Duty cycle of DC pulses: 10%*
Fig. 9.17: Threshold voltage of GaAs Gunn diodes as a function of temperature.

Fig. 9.18: $^{75}$As NMR signal intensity within and outside Gunn regime at 10K. Duty cycle of DC pulses: 4%
9.4 Discussion and Conclusion

As per the detailed theoretical calculations performed by Qi et al.\textsuperscript{140}, metallic GaAs and InP are expected to exhibit the spin Gunn effect beyond the Gunn threshold field for these semiconductors. Our experiments on highly doped GaAs and InP have shown that the Gunn regime is inaccessible in bulk samples of these semiconductors. Thin epitaxial layers are essential for these investigations. Furthermore, the surface area of the sample should be kept small in order to avoid high currents. However, measuring NMR on such small samples using standard NMR equipment is a challenging task.

We successfully reached the Gunn regime in commercial Gunn diodes and measured NMR despite the small volume of the samples. Good signal to noise ratio was achieved by using a modified FLASH-like pulse sequence. Within the accessible range of duty cycle and temperature, no clear effect of Gunn oscillations was observed on the NMR signal intensity. One or more of the following reasons may be responsible for this:

The thickness of the Gunn diode samples is 80 μm. However, the active region of a Gunn diode where Gunn oscillations occur is very thin, the rest being the thickness of the GaAs substrate on which this layer is grown. The exact width of the Gunn region is not known for these diodes. However, for K-band diodes operating at primary frequency, thickness can be estimated to be about 10 μm. This is 12.5% of the total diode thickness. Thus, only the NMR signal coming from 12.5% of the volume is expected to show any change in signal intensity when voltage exceeding Gunn threshold is applied. Furthermore, this percentage reduces to ~2% when we consider the fact that the NMR signal is measured from 6 diodes out of which only 1 diode enters the Gunn regime. Thus, the expected DNP can be observed in the settings mentioned above only if the DNP enhancement factors are of the order of ~100. We had shown in chapter 5 that DNP enhancement factors as large as ~500 may be achieved in InP. DNP effects of a similar scale are expected in GaAs Gunn diodes as well. Clearly, under the measurement conditions described in this chapter, the electron spin polarization and the resultant DNP appears to be much smaller.

Moreover, since the DNP always needs time to build up (~T\textsubscript{1}), Gunn oscillations should persist in the sample longer than the nuclear spin lattice relaxation time of nuclei for DNP to build up. As mentioned in the previous chapter, heating of semiconductor samples in presence of electric current cannot be completely avoided. Gunn diode samples have very small dimensions and hence much more severe heating of the
samples as compared to bulk GaAs wafers was encountered. The ohmic heating of the contacts does not allow use of duty cycle higher than 40% and application of voltage for long time period. Thus, complete DNP is not likely to build up in our samples under these conditions.

In light of the above mentioned factors, we conclude that more sensitive and faster detection techniques are needed for detection of the predicted spin Gunn effect. Some suggestions for future work are mentioned in the next section.

9.5 Outlook

Nuclear Magnetic Resonance is undoubtedly the most powerful analysis technique with widespread applications. This technique however suffers from a problem of relatively low sensitivity. Standard NMR requires number of nuclear spins to be typically of the order of $10^{14}$-$10^{16}$ for reasonable signal detection. Practical considerations limit the size of Gunn samples. The number of nuclei in a standard Gunn diode is just on the limit of detection and hence enhancement of sensitivity is paramount for DNP measurements described in this chapter. One of the most promising methods of NMR signal enhancement for such small samples is by use of microcoils\textsuperscript{141}. Solenoidal or single loop microcoils of dimensions <1mm have been used successfully by various groups for microfluid\textsuperscript{142} as well as solid state applications\textsuperscript{143}. Cooling of rf coils in cryoprobes will further enhance the signal detection capability.

Commercial Gunn diodes are manufactured by growing a thin epitaxial GaAs layer on a highly doped GaAs substrate. The thin layer (called active layer) is low doped and enters the Gunn regime at voltage greater than the threshold value. The substrate layer is highly doped and does not enter the Gunn regime. The spin Gunn effect is thus expected only from thin low doped GaAs layer. With standard NMR detection scheme, however, there is no way of separating the signal contribution from these two layers. GaAs Gunn diodes grown on a different substrate will be more suitable for spin Gunn effect detected via nuclear magnetic resonance.

The predicted spin Gunn effect is expected to result in spin polarized domains extending in space to a few microns in GaAs and InP. Spin polarization within these domains may be directly observed by means of localized techniques such as Faraday rotation, optically enhanced and detected NMR and magneto-optic Kerr effect. When there is a convincing electrical method of spin-polarization detection in nonmagnetic semiconductors, these spin-polarized pulses may be detectable directly in that way.
As was described in chapter 8, current flowing through GaAs wafers causes heating of the samples. Efficient heat sinks are thus needed to dissipate the heat generated. Commercial Gunn oscillators use a large piece of metal with huge surface area as a heat sink. This is hard to implement in our set-up since the sample lies inside the NMR coil which can accommodate only a small non-metallic heat sink. The sapphire heat sink (of dimension \( \approx 4 \times 2 \text{mm}^2 \)) used in our set up is clearly not adequate to dissipate heat generated beyond the Gunn threshold voltage. Water cooling or air cooling is also commonly used in Gunn oscillators. These methods are not suitable for NMR measurements at low temperatures. Thus, an efficient heat dissipation system which can be implemented within the NMR coil is needed for spin Gunn effect measurements described in this dissertation.
Chapter 10

Conclusion

In conclusion, our extensive NMR and double resonance measurements have highlighted the importance of electron-nuclear hyperfine coupling in silicon and III-V semiconductors. Strong hyperfine interaction, especially in the vicinity of localized electron centres, has been shown to play a critical role in electron and nuclear spin relaxation mechanisms. This has important pertinence in spintronic devices where long coherence times are desirable.

In contrast to some earlier observations, we have shown that dynamic nuclear polarization effects in these semiconductors arise mainly from localized electron centres. Interaction of conduction electrons with nuclear spins also appears to occur via these localized intermediaries. Through our NMR and double resonance measurements on semiconductors with varying doping concentration in a wide range of temperature, we have established the range of doping concentration and temperature conducive for DNP effects.

DNP effects have been shown to severely affect ESR line position and in some cases even result in lineshape distortions. Thus, our measurements have clearly pointed out that inclusion of these effects in precise ESR studies is indispensable.
We have shown that the electron spin system in low doped InP can be polarized by means of electric current which is consistent with model predictions in zinc-blende semiconductors. We measured the enhancement of nuclear polarization resulting from relaxation of electron polarization to equilibrium via the nuclear spin system. The maximum DNP enhancement factor was measured to be ~1.5. Much higher enhancement is expected if heating due to current can be avoided.

From our investigations of possible spin Gunn effect in InP and GaAs, we conclude that owing to high electrical conductivity, it is practically very hard to reach Gunn regime in metallic bulk samples of these semiconductors. Thin epitaxial layers with small surface area are therefore essential for these investigations. Despite the small volume of commercial Gunn diode samples, we successfully measured NMR on these samples within the Gunn regime. However, under the experimental conditions used in this study, the electron spin polarization appears to be much smaller than the theoretical prediction. The resulting DNP effects are therefore below the detection limits of NMR. Localized measurement techniques such as Faraday rotation, optically enhanced and detected NMR and magneto-optic Kerr effect seem to be better suited for detection of spin polarized domains as compared to bulk technique such as standard NMR. Moreover, it was observed that generation of charge Gunn domains (and hence spin Gunn domains) results in severe heating of the Gunn diode. Efficient heat sinks are therefore essential for investigation of the predicted spin Gunn effect in semiconductors.
Summary

Motivation

Recent discoveries in spintronics have triggered a quest for spintronics without magnetism. The ultimate goal of this branch of spintronics is to realize an “all electric spintronic device”. Spin-Orbit effects in semiconductors provide a promising possibility to generate and manipulate carrier spins without involving any ferromagnetism. Though the effects of spin-orbit coupling such as the spin Hall effect and the current induced spin polarization have been seen experimentally in a variety of semiconductors, a thorough understanding of these effects is still lacking. Furthermore, spin decoherence time of electrons in III-V semiconductors is known to be severely affected by the interaction with nuclear spins. Thus, for spintronics devices, the role played by the nuclei in electron spin decoherence and dynamic nuclear polarization processes needs to be understood.

Analogous to the spin Hall effect, the “spin Gunn effect” has been proposed recently in III-V semiconductors. A small spin polarization (created either by a random thermal fluctuation or spin-orbit effects) is expected to grow and lead to spin polarized domains within the Gunn regime. If demonstrated experimentally, spin Gunn effect will open a wide range of possibilities in the field of spintronics.

The goal of this work was to investigate and understand the mechanism of current-induced DNP and possible existence of spin Gunn effect in III-V semiconductors such as GaAs and InP.

Critical Doping and Temperature Requirements for DNP

Dynamic nuclear polarization in semiconductors depends very strongly both on the electron concentration in the conduction band as well as on the concentration of localized electron centres. Furthermore, for dynamic nuclear polarization to exist, strong hyperfine coupling (and concomitant nuclear relaxation via electrons) is a crucial requirement. Thus, before commencing a systematic study of DNP, the determination of electron concentrations and temperature ranges conducive to the existence of DNP effects in semiconductors is imperative.

For this purpose, the temperature dependence of the resistivity and the nuclear spin relaxation rates was studied in InP and GaAs samples with varying doping concentrations. Whereas the temperature dependence of the resistivity clarifies the extent of localization of electrons, the
temperature dependence of nuclear spin lattice relaxation elucidates the dominant mechanism of nuclear spin relaxation for various nuclei in InP and GaAs. Electrical contacts were fabricated on semiconductor wafers by evaporating thin Au-Ge stripes. The thickness of the stripes was limited to ~50nm in order not to block RF at the NMR frequency (58MHz). This enabled NMR as well as electrical measurements on these samples.

It was observed that just-metallic samples of InP ($n=7 \times 10^{15}$ cm$^{-3}$) and GaAs ($n=2.5 \times 10^{16}$ cm$^{-3}$) showed variable range hopping type of conduction ($\sigma=\exp(-\sqrt{T/L})$) at temperatures lower than about 30K. Electron hopping results in motionally narrowed ESR lines and favours Overhauser type of dynamic nuclear polarization in these semiconductors. Semi-insulating samples of InP and GaAs, on the other hand, showed carrier freeze-out effects and hence resistivity measurements were not possible at low temperatures.

Nuclear spin lattice relaxation rates for all the nuclei in InP and GaAs were measured in the temperature range 8K-300K. In metallic as well as just metallic samples at $T>20K$, the $^{69}$Ga and $^{75}$As relaxation times were seen to increase approximately with $1/T^2$ dependence. This is a signature of two phonon quadrupolar relaxation. In the temperature range 8K-20K, the measured $T_1$ showed Korringa type relaxation (relaxation rate proportional to temperature). This confirms that relaxation via hyperfine coupling with electrons is the dominant relaxation mechanism at low temperatures ($<20K$) in metallic and just metallic GaAs. In the Korringa regime, the relaxation rate ($1/T_1$) is expected to be proportional to $n^{2/3}$ where $n$ is the electron concentration. As a result, the relaxation rate in metallic GaAs ($n=2.1 \times 10^{18}$ cm$^{-3}$) should be about 10 times faster than that of just metallic GaAs sample ($n=2.5 \times 10^{16}$cm$^{-3}$). The observed ratio is however 3. This suggests that the nuclear spin lattice relaxation in just metallic sample in the temperature range 8K-15K is not by conduction electrons but by means of interaction between localized electrons and its neighbouring nuclear spins in combination with spin diffusion to the bulk nuclei.

$^{115}$In nuclei in metallic InP showed a clear quadrupolar type relaxation at $T>50K$ and Korringa type relaxation at $T<50K$. $^{31}$P nuclei show Korringa relaxation in the entire temperature range. This is expected since $^{31}$P is a spin $1/2$ nucleus and hence cannot undergo quadrupolar relaxation. In undoped InP sample, $^{115}$In nuclei showed quadrupolar relaxation in almost the entire temperature range measured except for a very slight deviation at $T<10K$. The $^{31}$P relaxation rate, on the other hand, showed a $T^{1/2}$ behaviour consistent with nuclear spin lattice relaxation via electrons in semiconductors below the metal-insulator transition.
From the resistivity and relaxation rate measurements described above we conclude that low doped GaAs and InP at low temperatures (<20K) exhibit hopping conduction between localized states and strong hyperfine coupling effects. They are, thus, favourable systems where Overhauser type of dynamic nuclear polarization processes are likely to be operating.

**InP: ESR and Overhauser Measurements in X Band**

ESR signals of almost Lorentzian lineshape and linewidth ~1.8Gauss were observed from the undoped InP sample \( (n=7 \times 10^{15} \text{cm}^{-3}) \). Such motionally narrowed Lorentzian ESR lineshapes are expected for completely or partially delocalized electrons moving in overlapping shallow donor orbits and impurity bands. The ESR line position and linehape showed a dependence on microwave power due to DNP effects. By strong ESR saturation, the nuclear polarization is enhanced through hyperfine interaction between electrons and nuclear spins, leading to a shift of the ESR line to lower external field. This shift is known as the Overhauser shift. The subsequent recovery of the nuclear polarization to the thermal equilibrium value shifts the ESR line back to the original position.

For measurement of the Overhauser shift in InP, ESR saturation was carried out by means of a slow downward magnetic field sweep at high microwave power. The resultant Overhauser shift was measured to be about 45Gauss at \( P_{\mu w}=16\text{mW} \). Subsequent fast ESR scans were then carried out at very low microwave power in order to follow the recovery of nuclear polarization. Since the recovery of nuclear polarization occurs with a time constant \( T_1 \) (nuclear spin lattice relaxation) at that temperature, the ESR line shifts back to its thermal equilibrium position on the same time scale. The \( T_1 \) of \(^{115}\text{In}\) nuclei responsible for the Overhauser shift was determined from the plot of ESR line position vs. time as 105s at 8K.

For the double resonance measurement of the Overhauser shift, the nuclear spin polarization was reduced to zero by application of a saturating RF field at the NMR frequency of the respective nucleus. The dependence of Overhauser shift on ESR and RF saturation was measured and DNP parameters for both \(^{115}\text{In}\) and \(^{31}\text{P}\) nuclei were determined as:

| Nucleus | \( V_{\text{max}} \) | \( V \) | \( f \) | \( T_1 \) (s) | \( |\Psi(0)|^2 \) (cm\(^{-3}\)) |
|---------|-----------------|-------|-----|-----------|-----------------|
| \(^{115}\text{In}\) | 1796 | 257 | 0.143 | 105 | \( 6.79 \times 10^{25} \) |
| \(^{31}\text{P}\) | 977 | 454 | 0.465 | 175 | \( 3.18 \times 10^{25} \) |
where $V_{\text{max}}$ is the maximum DNP enhancement possible (given by the ratio of electron and nuclear gyromagnetic ratios), $V$ is the measured DNP enhancement factor, $f$ is the leakage factor defined by the ratio of relaxation rate via the contact hyperfine interaction to the total relaxation rate and $|\Psi(0)|^2$ is the density of conduction electron at a particular nuclear site. From the above mentioned measurements, one may conclude:

- Huge DNP enhancements (by a factor of 257 and 454 for $^{115}\text{In}$ and $^{31}\text{P}$ respectively) are possible in undoped InP at 8K.
- Nuclear spin lattice relaxation times of $^{115}\text{In}$ and $^{31}\text{P}$ nuclei responsible for Overhauser shift were measured to be about 105s and 175s respectively. These values are at least an order of magnitude lower than the $T_1$ times measured by standard NMR technique. This can be explained by considering the extended wavefunction of a shallow donor. The nuclei closest to the donor experience the strongest hyperfine interaction and hence have the fastest relaxation rates. As the distance of the nuclei from the donor increases, the hyperfine interaction decreases and hence the nuclear spin lattice relaxation rate becomes slower. Standard NMR technique measures the $T_1$ of bulk nuclei whereas the Overhauser technique picks out nuclei closest to the localized electron centre.
- The conduction electron is unequally shared between $^{115}\text{In}$ and $^{31}\text{P}$, with enhanced probability at the $^{115}\text{In}$ nucleus.

**GaAs: ESR Measurements**

ESR measurements on n-type GaAs ($n=1.2 \times 10^{15}\text{cm}^{-3}$) were performed using a broadband (5-40GHz) ESR spectrometer combined with a superconducting magnet (up to 10T). A broad ($\sim$0.4T) and asymmetric ESR line was observed at $g_e=-0.4215$ at $1\mu\text{W}$ microwave power. At higher microwave power (2$\mu\text{W}$), a much broader ESR line (1T) was observed. This broadening of the ESR line is due to Overhauser shift induced by dynamic nuclear polarization. The asymmetry of ESR lines and its dependence on microwave power clearly indicate that strong hyperfine coupling (and hence DNP) exists in low doped GaAs.

**Si:P: ESR and Overhauser Measurements in X Band**

Overhauser shift measurements were performed on phosphorus doped silicon ($3 \times 10^{18}\text{cm}^{-3}$) by means of a double resonance technique. The Overhauser signal from $^{29}\text{Si}$ is inverted (shift towards negative field) as compared to the $^{115}\text{In}$ signal due to negative $\gamma$ of $^{29}\text{Si}$ nuclei. The negative Overhauser shift by $^{29}\text{Si}$ nuclei clearly shows that the Fermi contact hyperfine interaction (and not the dipolar interaction) is the dominant
interaction responsible for dynamic nuclear polarization of $^{29}$Si. Furthermore, the lineshape of the Overhauser signal was observed to be asymmetric. The asymmetry is attributed to the distribution of distance of $^{29}$Si nuclei from P donors leading to a distribution in hyperfine interaction (and hence the Overhauser shift and the paramagnetic shift). The dependence of Overhauser shift on ESR and RF saturation was measured and DNP parameters for $^{29}$Si were determined as:

| Nucleus | $V_{max}$ | $V$ | $f$ | $K$(ppm) | $|\Psi(0)|^2$(cm$^{-3}$) |
|---------|-----------|-----|-----|----------|--------------------------|
| $^{29}$Si | -3305 | -31.2 | 0.009 | 710.6 | 7.45×10$^{23}$ |

The central nucleus ($^{31}$P in this case) is strongly coupled to the electron. This poses a problem in detection of the central nucleus due to extremely short relaxation time. In order to saturate the NMR transition of the central nucleus, strong RF fields and a high quality factor of the cavity is needed. The Overhauser shift due to central nucleus can however be estimated by measuring the integral shift (total shift of the ESR line position after saturation) and subtracting the contribution from $^{29}$Si nuclei. In our measurements, the Overhauser shift due to $^{31}$P nuclei was estimated to be about 436mG (at complete ESR saturation).

**Modeling and Simulation of DNP Parameters**

In order to understand the interactions which are responsible for creation of dynamic nuclear polarization and Overhauser shifts in semiconductors, a quantitative model consisting of a homogenous distribution of donors in a semiconductor (wherein each electron localized at a donor centre interacts with the surrounding nuclei via contact hyperfine interaction) was developed. The wavefunction of the electron centre was computed using the effective mass theory. Knowing the density of the electron wavefunction at radius (r), the strength of Fermi contact type hyperfine interaction experienced by a nucleus at distance r was calculated. DNP related parameters such as nuclear spin lattice relaxation time ($T_{1e}$), paramagnetic shift (K in ppm), Overhauser shift ($B_n$) and RF saturation factor ($s_{RF}$) were then computed by a numerical integration over the entire extension of the wavefunction.

The simulated values were reasonably close to the experimentally measured values. In order to improve the precision of simulations, other mechanisms operating in these semiconductors such as spin diffusion, overlap of electron wavefunction and subsequent electron hopping must be included in the model.
Current-Induced Dynamic Nuclear Polarization in InP and GaAs

InP and GaAs both have zinc-blende crystal structure and are thus expected to show current induced electron spin polarization owing to the inversion asymmetry of the lattice. The electron spin system when driven out of equilibrium is known to give rise to DNP through hyperfine mediated processes in these semiconductors. Electric current is thus expected to induce DNP effects in InP and GaAs. Current induced DNP was investigated in InP and GaAs by passing electric current through semiconductor wafers and measuring the nuclear polarization by means of standard NMR experiments.

Undoped InP \( (n=7 \times 10^{15}\text{cm}^{-3}) \) showed a reduction in NMR signal intensity with increase in current strength. A part of the reduction was attributed to heating of the semiconductor wafers due to current. After subtracting the heating effect from the measured NMR signal reduction, the net effect due to current induced dynamic nuclear polarization was obtained. A net positive enhancement of \(^{115}\text{In}\) NMR signal intensity (to about 50%) was observed at current close to 10mA at 8K. Beyond this current intensity, DNP enhancement started to reduce. This was attributed to a rise in temperature at higher current. Since \(^{115}\text{In}\) nuclei undergo quadrupolar relaxation at \( T>15K \), an increase in temperature means a greater tendency to undergo quadrupolar relaxation and thus lower dynamic nuclear polarization.

A similar measurement for \(^{31}\text{P}\) in InP showed a much lower \(^{31}\text{P}\) DNP enhancement as compared to \(^{115}\text{In}\). A likely reason for low DNP enhancement for \(^{31}\text{P}\) is that \( T_1 \) of \(^{31}\text{P}\) nuclei is longer than \(^{115}\text{In}\) nuclei at 8K (\( T_1(^{115}\text{In})=527s, T_1(^{31}\text{P})=1420s \)). Therefore, current pulses need to be applied for a much longer duration in order to obtain complete DNP for \(^{31}\text{P}\) nuclei. However, due to heating of the sample induced by dc current, the nuclear polarization was reduced before the complete build up of DNP. Thus, the observed DNP enhancement was smaller for \(^{31}\text{P}\) as compared to \(^{115}\text{In}\) nuclei.

In order to investigate the time scale on which the observed current-induced DNP builds up, measurements were performed where the enhancement factors were measured for different DC periods (denoted by \( t \)) for a fixed current intensity. The net DNP effect was seen to increase with the duration of DC pulses \( (t) \) initially. However, longer duration of DC current pulses caused a temperature increase resulting in reduction of signal intensity. For building up of complete DNP, the duration time of DC pulses should be at least \( \sim 3T_1 \) where \( T_1 \) is the nuclear spin lattice relaxation time. Due to heating of the sample, the nuclear spin polarization was reduced even before the complete build up of dynamic
nuclear polarization occurred. Thus, one may conclude that the DNP enhancement factor for $^{115}\text{In}$ at 8K is certainly more than the observed value of 1.5.

$^{115}\text{In}$ DNP enhancement at 25K was measured to be much smaller than the corresponding value at 8K. In n-type zinc-blende semiconductors, D'yakonov and Perel and Elliot Yafet mechanisms of electron spin relaxation dominate. Since the efficiency of both these mechanisms is known to increase with temperature, electron spin relaxation time decreases with increase in temperature. It appears that short spin coherence times of III-V semiconductors do not allow DNP effects to build up at higher temperatures. Furthermore, our measurements of temperature dependence of nuclear spin lattice relaxation in undoped InP showed that quadrupolar relaxation is the dominant mode of nuclear relaxation at T>15K. Thus, DNP is expected to become much less efficient at T>15K.

Similar measurements of current-induced DNP were performed on low doped GaAs wafers. Insulating GaAs ($n = 1.2 \times 10^{15} \text{cm}^{-3}$) showed microwave induced DNP effects in ESR measurements and hence is expected to show current-induced DNP as well. However, carrier freeze out starts to occur in this sample at 150K and hence current induced DNP measurements were not possible at lower temperature. No net DNP effects were observed in just-metallic GaAs ($n = 2.5 \times 10^{16} \text{cm}^{-3}$) samples. The doping concentration of this sample appears to be higher than the critical doping range where DNP processes build up. GaAs samples with concentration close to MIT ($n \approx 3.0 \times 10^{15} \text{cm}^{-3}$) must be used for current-induced DNP experiments.

More precise and conclusive measurements can be performed on low doped InP if heating effects can be avoided. Better electrical contacts must be tried in order to alleviate current-induced heating. Once the heating effects are avoided, measurements can be performed to investigate the time scale of DNP build-up processes as well as effect of electric current on nuclear spin lattice relaxation rates. These measurements are likely to elucidate the role of itinerant and localized electron in the DNP mechanism. Furthermore, reduction of heating effects will enable measurement of current-induced DNP enhancement in $^{31}\text{P}$ nuclei as well. Due to stronger hyperfine interaction and higher leakage factor (no quadrupolar relaxation), $^{31}\text{P}$ is expected to show much higher DNP enhancement as compared to $^{115}\text{In}$. 
Summary

**Spin Gunn Effect**

The difference in electron mobility in the bottom of the conduction band (lower valley) and the first higher subband (upper band) causes the standard Gunn effect in some direct band gap semiconductors such as GaAs and InP. The electron mobility is however spin dependent in these semiconductors. Thus, a small spin polarization (created either by a random thermal fluctuation or spin-orbit effects) is expected to grow and lead to spin polarized domains. This is termed as the "Spin Gunn Effect".

Within a spin Gunn domain, the electron spin system is driven out of equilibrium and has a tendency to relax to the equilibrium. In a situation where electrons are strongly coupled to the nuclei, the transitions of electron spin system towards thermal equilibrium are expected to dynamically polarize nuclear spins. We performed standard NMR measurements on GaAs and InP wafers of different doping concentrations in the presence of DC pulses in order to investigate the effect of spin polarized domains on the nuclear polarization.

It was practically impossible to reach the Gunn regime in metallic bulk samples of GaAs and InP due to high conductivity. In low doped GaAs samples, the Gunn regime could not be reached possibly due to high resistance of contacts. We successfully reached the Gunn regime in commercial Gunn diodes made of GaAs and measured NMR despite the small volume of the samples. A good signal to noise ratio was achieved by using a modified FLASH-like pulse sequence. Within the accessible range of duty cycle and temperature, no clear effect of Gunn oscillations was however observed on the NMR signal intensity.

From our investigations of possible spin Gunn effect in InP and GaAs, we conclude that owing to high electrical conductivity, Gunn regime is inaccessible in metallic bulk samples of these semiconductors. Thin epitaxial layers with small surface area are thus essential for these investigations. Under the experimental conditions used in this study, the electron spin polarization appears to be much smaller than the theoretical prediction. The resulting DNP effects are therefore below the detection limits of NMR. Localized measurement techniques such as Faraday rotation, optically enhanced and detected NMR and magneto-optic Kerr effect are better suited for detection of spin polarized domains as compared to bulk technique such as standard NMR. Also, it was observed that generation of charge Gunn domains (and hence spin Gunn domains) results in heating of the Gunn diode. Efficient heat sinks are therefore essential for investigation of the spin Gunn effect in semiconductors.
Zusammenfassung

Motivation


Das Ziel der vorliegenden Arbeit war, die Grundlagen der strominduzierten DNP und die mögliche Existenz des Spin-Gunn-Effektes in III-V Halbleitern zu untersuchen und zu verstehen.

Kritische Dotierungs- und Temperatur-Anforderungen für DNP

Zusammenfassung

Zu diesem Zweck wurden die Temperaturabhängigkeit des Widerstandes und der Kernspin-Relaxationsraten in InP und GaAs Proben unterschiedlicher Dotierungskonzentrationen untersucht. Während die Temperaturabhängigkeit des Widerstandes den Einfluss der Lokalisierung der Elektronen aufklärt, erhellt die Temperaturabhängigkeit der Kernspinrelaxation die dominierenden Prozesse der Kernspinrelaxation für die verschiedenen Kerne in InP und GaAs. Durch Aufdampfen dünner Au-Ge Streifen auf die Halbleiter Scheiben wurden elektrische Kontakte angebracht. Die Dicke dieser Streifen wurde auf ca. 50 nm eingeschränkt, um nicht die Radiofrequenzfelder bei der NMR-Frequenz (58MHz) zu blockieren. Dies ermöglichte sowohl NMR-Messungen als auch elektrische Messungen an diesen Proben.

Beobachtet wurde, dass Proben mit gerade metallischem Verhalten von InP (n=7x10^{15}cm^{-3}) und GaAs (n=2.5x10^{16}cm^{-3}) eine Leitfähigkeit vom Typ "variable range hopping" ($\sigma = \exp(-\frac{1}{T})$) bei Temperaturen unterhalb etwa 30K zeigten. Elektronenhüpfen führt zu bewegungsverschmälerten ESR-Linien und begünstigt eine Dynamische Kernspinpolarisation vom Overhauser-Typ in diesen Halbleitern. Bei höheren Temperaturen ändert sich der Widerstand exponentiell mit 1/T wegen der der thermischen Aktivierung von lokализierten Donatoren. Auf der anderen Seite zeigten semi-isolierende Proben von InP und GaAs Ausfriereffekte der Ladungsträger, und verhinderten deshalb Widerstandsmessungen bei tiefen Temperaturen.

Die Kernspinrelaxationsraten aller Kerne in InP und GaAs wurden im Temperaturbereich 8K–300K gemessen. Sowohl in metallischen als auch gerade metallischen Proben bei T>20K beobachtete man einen Anstieg der Relaxationszeiten mit einer angenäherten 1/T^2 Abhängigkeit für die ^69Ga und ^75As Kerne. Dies ist die Signatur von quadrupolärer Relaxation über einen Zweiphononen-Prozess. Im Temperaturbereich 8K–20K zeigten die gemessenen $T_1$ eine Relaxation vom Korringa-Typ (Relaxationsrate proportional zur Temperatur). Dies bestätigt, dass die Relaxation über die Hyperfeinkopplung der dominante Relaxations-Mechanismus bei tiefen Temperaturen (<20K) in den metallischen und gerade metallischen Proben ist. Im Korringa-Bereich erwartet man erwartet man die Relaxationsrate ($1/T_1$) proportional zu $n^{2/3}$, wobei n die Elektronenkonzentration ist. Die Relaxationsrate in metallischem GaAs (n=2.1x10^{18}cm^{-3}) sollte deshalb etwa 10 mal größer als die Rate in den gerade metallischen GaAs-Proben (n=2.5x10^{16}cm^{-3}) sein. Das beobachtete Verhältnis ist allerdings 3. Dies legt nahe dass die Spin-Gitter-Relaxation in gerade metallischen Proben im Temperaturbereich 8K – 15K nicht durch Leitungselektronen bewirkt wird, sondern durch eine Wechselwirkung zwischen lokalisierten Elektronen und den
Die \(^{115}\text{In}\) Kerne in metallischen InP zeigten klar eine quadrupolare Relaxation für \(T>50\,\text{K}\) und eine Korringa-Relaxation für \(T<50\,\text{K}\). Die \(^{31}\text{P}\) Kerne zeigen dagegen eine Korringa-Relaxation im gesamten Temperaturbereich. Dies erwartet man auch, denn \(^{31}\text{P}\) ist ein Spin \(\frac{1}{2}\) Kern und unterliegt damit nicht der quadrupolaren Relaxation. Im der undotierten InP Probe zeigen die \(^{115}\text{In}\) Kerne eine quadrupolare Relaxation fast im gesamten Temperaturbereich mit einer sehr kleinen Abweichung bei \(T<10\,\text{K}\). Andererseits zeigt die \(^{31}\text{P}\) Relaxationsrate ein \(T^{1/2}\) Verhalten im Einklang mit einer Kernspinrelaxation über Elektronen in Halbleitern unterhalb des Metall-Isolator-Übergangs.

Aus den oben beschriebenen Messungen des Widerstandes und der Relaxationsraten schließen wir, dass niedrig dotierte GaAs und InP Halbleiter bei tiefen Temperaturen (<20K) Hüpfleitfähigkeit zwischen lokalisierten Zuständen und starke Hyperfeinkopplungs-Effekte aufweisen. Sie sind deswegen günstige Systeme, bei denen wahrscheinlich Dynamische Kernspinpolarisations-Prozesse vom Overhauser-Typ auftreten.

**InP: ESR und Overhauser Messungen im X-Band**


Zur Messung der Overhauser-Verschiebung in InP wurde die ESR-Sättigung durch einen langsamen Magnetfeldsweep in Richtung kleinerer Feldstärke bei hoher Mikrowellenleistung ausgeführt. Die resultierende Overhauser-Verschiebung betrug 45 Gauß bei \(P_{\text{mw}}=16\,\text{mW}\). Nachfolgende schnelle ESR-Messungen wurden bei sehr kleinen Mikrowellenleistungen ausgeführt, um den Abbau der Kernspinpolarisation zu beobachten. Da
dieser Abbau der Kernspinpolarisation mit einer temperaturabhängigen Zeitkonstanten $T_1$ (Spin-Gitter-Relaxationszeit) erfolgt, schiebt sich die ESR-Linie auf dieser Zeitskala zurück auf die Position im thermischen Gleichgewicht. Die $T_1$-Zeit der $^{115}$In Kerne, welche für die Overhauser-Verschiebung verantwortlich sind, wurde aus der Auftragung der ESR-Linienposition gegen die Zeit als 105 s bei 8K bestimmt.

Für die Doppelresonanz-Messungen der Overhauser-Verschiebung wurde die Kernspinpolarisation durch die Anwendung eines die NMR sättigenden Radiofrequenzfeldes mit der NMR-Frequenz des betrachteten Kernes auf Null reduziert. Die Abhängigkeit der Overhauser-Verschiebung von der ESR-Sättigung und der NMR-Sättigung wurde gemessen und die DNP-Parameter für $^{115}$In und $^{31}$P wurden wie folgt bestimmt:

| Parameter der Dynamischen Kernspinpolarisation für InP bei 8K |
|-----------------|------|--------|----------|------------|
| Nucleus         | $V_{\text{max}}$ | $V$    | $f$      | $T_1$ (s)  | $|\Psi(0)|^2$ (cm$^{-3}$) |
| $^{115}$In       | 1796 | 257    | 0.143    | 105        | $6.79 \times 10^{25}$ |
| $^{31}$P         | 977  | 454    | 0.465    | 175        | $3.18 \times 10^{25}$ |

Dabei ist $V_{\text{max}}$ die maximal mögliche DNP-Verstärkung (der Quotient der gyromagnetischen Verhältnisse des Elektrons zum Kern), $V$ ist der gemessene DNP-Verstärkungsfaktor, $f$ ist der Leckfaktor (definiert als das Verhältnis der Relaxationsrate über die Kontakt-Hyperfeinwechselwirkung zur Gesamtrelexationsrate) und $|\Psi(0)|^2$ ist die Aufenthaltsdichte der Leitungselektronen an der betreffenden Kernposition. Aus den oben genannten Messungen können wir folgendes schließen:

- Riesige DNP-Verstärkungsfaktoren (257 für $^{115}$In und 454 für $^{31}$P) sind in undotiertem InP bei 8K möglich.
- Die Kernspinrelaxationszeiten der $^{115}$In und $^{31}$P Kerne, welche für die Overhauser-Verschiebung verantwortlich sind, wurden zu 105s und 175s bestimmt. Diese Werte sind mindestens eine Größenordnung kürzer als die $T_1$-Zeiten aus Standard NMR Messungen (an den gleichen Proben). Dies kann durch die Berücksichtigung der ausgedehnten Wellenfunktion der flachen Donatoren erklärt werden. Die den Donatoren räumlich naheliegenden Kerne unterliegen der stärksten Hyperfein-Wechselwirkung und haben infolgedessen die schnellsten Relaxationsraten. Mit zunehmender Entfernung der Kerne vom Donator sinkt die Hyperfein-Wechselwirkung und die Kernspinrelaxationsrate wird kleiner. Die Standard-NMR mißt das $T_1$ aller Kerne im Volumen, während die Overhauser-
Verschiebungs-Methode die Kerne nahe an den lokализierten Elektronenzentren herausgreift.

- Das Leitungselektron wird ungleich zwischen den $^{115}$In und den $^{31}$P Positionen "aufgeteilt" und zwar mit einer höheren Aufenthaltswahrscheinlichkeit am $^{115}$In Kern.

**GaAs: ESR-Messungen**

ESR-Messungen an den n–GaAs Proben ($n=1.2 \times 10^{15}$cm$^{-3}$) wurden mit einem Breitband (5-40GHz) ESR-Spektrometer kombiniert mit einem Supraleitenden Magneten (bis zu 10T) durchgeführt. Eine breite (~0.4T) und asymmetrische ESR-Linie wurde bei $g = 0.4215$ bei der Messung mit 1µW Mikrowellenleistung beobachtet. Bei höherer Mikrowellenleistung (2µW) wurde eine viel breitere ESR-Linie (1T) beobachtet. Diese Verbreiterung der ESR-Linie liegt an der durch die Dynamische-Kernspinpolarisation bedingten Overhauser-Verschiebung. Die Asymmetrie der ESR-Linie und die Abhängigkeit von der Mikrowellenleistung zeigt klar, dass in niedrig dotierten GaAs eine starke Hyperfein-Kopplung (und eine starke DNP) vorliegt.

**Si:P: ESR- und Overhauser-Verschiebungsmessungen im X-Band**

Overhauser-Verschiebungsmessungen wurden in Phosphor-dotiertem Silizium ($3 \times 10^{18}$cm$^{-3}$) mit Hilfe der Doppelresonanztechnik durchgeführt. Das Overhauser-Verschiebungssignal von $^{29}$Si ist bezogen auf das Signal von $^{115}$In invertiert (Verschiebung in Richtung negatives Feld). Dies liegt an dem negativen $\gamma$ des $^{29}$Si-Kerns. Die negative Overhauser-Verschiebung durch die $^{29}$Si-Kerne zeigt klar, dass die Fermi-Kontakt Wechselwirkung (und nicht die Dipolar-Wechselwirkung) die dominante Wechselwirkung ist, welche für die Dynamische Kernspinpolarisation der $^{29}$Si verantwortlich ist. Des Weiteren wurde eine asymmetrische Linienform der Overhauser-Verschiebung beobachtet. Diese Asymmetrie wird der Abstandsverteilung der $^{29}$Si-Kerne von den P-Donatoren zugeschrieben. Diese Verteilung führt zu einer Verteilung der Hyperfeinwechselwirkungen (und damit zu einer Verteilung der Overhauser-Verschiebung und der Paramagnetischen Verschiebung). Die Abhängigkeit der Overhauser-Verschiebung von der ESR- und NMR-Sättigung wurde gemessen und die DNP Parameter für $^{29}$Si wie folgt bestimmt:

| Parameter der Dynamischen Kernspinpolarisation für Si:P bei 10K |
|-------------------|----------------|--------|---------|------------------|
| Nucleus | $V_{\text{max}}$ | $V$   | $f$    | $K$(ppm) | $|\Psi(0)|^2$(cm$^{-3}$) |
| $^{29}$Si | -3305 | -31.2 | 0.009 | 710.6 | $7.45 \times 10^{23}$ cm$^{-3}$ |

**Modellierung und Simulation der DNP-Parameter**

Um die für die Erzeugung von Dynamischer Kernspinpolarisation und die Overhauserverschiebung in Halbleitern verantwortlichen Wechselwirkungen zu verstehen, wurde ein quantitatives Modell entwickelt. Dieses Modell nimmt eine homogene Verteilung von Donatoren im Halbleiter an, und jedes an einem Donator-Zentrum lokalisierte Elektron wechselwirkt mit den umgebenden Kernspins über die Kontakt-Hyperfein-Wechselwirkung. Die Wellenfunktion des Elektronenzentrums wurde mit der effektiven Massentheorie berechnet. Aus der Kenntnis der Aufenthaltswahrscheinlichkeit der Elektronenwellenfunktion beim Radius r wurde die Stärke der Fermi-Kontakt-Wechselwirkung auf einen Kern in der Entfernung r berechnet. Die die DNP betreffenden Parameter wie Kernspin-Gitter-Relaxationszeit ($T_{1e}$), Paramagnetische Verschiebung ($K$ in ppm), Overhauser-Verschiebung ($B_n$) und RF-Sättigungs-Faktor ($s_{RF}$) wurden dann durch eine numerische Integration über die gesamte Ausdehnung der Wellenfunktion berechnet.

Die so simulierten Werte waren vernünftig nahe an den experimentell gemessenen Werten. Um die Präzision dieser Simulationen zu erhöhen, muss man weitere in diesen Halbleitern vorhandene Mechanismen wie Spindiffusion, Überlapp der Elektronenwellenfunktion und daraus folgendes Hüpfen der Elektronen in dieses Modell einbeziehen.

**Strominduzierte dynamische Kernspinpolarisation in InP und GaAs**

InP und GaAs besitzen die Zinkblenden-Kristallstruktur, und deshalb erwartet man aufgrund der Inversionsasymmetrie der Gitterstruktur, dass beiden Strukturen strominduzierte Elektronenspin–Polarisation zeigen. Es ist bekannt, dass das Elektronenspin - System, wenn es aus dem Gleichgewicht gebracht wird, DNP durch Hyperfeinwechselwirkung erzeugt. Deshalb wird vermutet, dass elektrischer Strom DNP - Effekte auch in InP und GaAs bewirkt. Untersucht wurde dieser strominduzierte DNP - Effekt in InP und GaAs, indem elektrischer Strom durch
Halbleiterwafer geschickt und die Kernspinpolarisation mithilfe von Standard NMR-Experimenten gemessen wurde.


Eine ähnliche Messung für ^{31}P in InP zeigte eine viel kleinere ^{31}P DNP Verstärkung, verglichen mit ^{115}In. Wahrscheinlich ist der Grund für die geringere ^{31}P DNP Verstärkung, dass bei 8K die T1-Zeit der ^{31}P Kerne länger ist als die der ^{115}In Kerne (T1(^{115}In)=527s, T1(^{31}P)=1420s). Um einen vollständigen DNP - Effekt für ^{31}P Kerne zu erhalten, muss man deshalb über einen viel längeren Zeitraum Strompulse anlegen. Im Experiment hatte allerdings die Erwärming der Probe durch den angelegten Gleichstrom zur Folge, dass die Kernspinpolarisation bereits verringert wurde, bevor der DNP – Effekt sich vollständig ausgebildet hatte. Somit fiel die beobachtete DNP Verstärkung für ^{31}P kleiner aus als bei ^{115}In.

Um zu untersuchen, auf welcher Zeitskala sich der beobachtete strominduzierte DNP –Effekt aufbaut, wurden Messungen durchgeführt, bei denen die Verstärkungsfaktoren für verschiedenen DC Perioden (bezeichnet mit τ) bei einer gleichbleibenden Stromstärke gemessen wurden. Man beobachtete, dass der resultierende DNP - Effekt anfangs mit der Dauer der DC Pulse (τ) zunahm. Länger andauernde Gleichstrompulse verursachten jedoch einen Temperaturanstieg, der eine Verminderung der Signalstärke zur Folge hatte. Um den vollständigen DNP - Effekt aufzubauen sollte die Dauer der DC Pulse mindestens ~ 3T1 sein, wobei T1 die Kernspin-Gitter-Relaxationszeit ist. Durch die Erwärmung der Probe wurde die Kernspinpolarisation sogar schon verringert bevor sich die dynamische Kernspinpolarisation vollständig ausgebildet hatte. Daraus lässt sich schließen, dass der DNP Verstärkungsfaktor für ^{115}In bei 8K mit Sicherheit über dem beobachteten Wert von 1.5 liegen muss.

Ähnliche Messungen des strominduzierten DNP - Effekts wurden an niederdotierten GaAs Wafern durchgeführt. Isolierendes GaAs ($n=1.2\times10^{15} \text{ cm}^{-3}$) zeigte in ESR Messungen mikrowellen-induzierte DNP – Effekte. Dies lässt vermuten, dass sich strominduzierte DNP Effekte ebenfalls beobachten lassen. Jedoch frieren bei Temperaturen unterhalb von 150K in diesen Proben die Ladungsträger aus (carrier freeze out) und dadurch sind Messungen des strominduzierten DNP - Effekts bei niedrigeren Temperaturen nicht möglich. Es wurden keine resultierenden DNP - Effekte in gerade metallischem GaAs ($n=2.5\times10^{16} \text{ cm}^{-3}$) beobachtet. Die Dotierungskonzentration dieser Probe scheint höher als die kritische Grenze zu sein, bis zu der DNP-Prozesse auftreten. GaAs Proben mit einer Konzentration nahe am Metall-Isolator-Übergang ($n\approx3.0\times10^{15} \text{ cm}^{-3}$) müssen für strominduzierte DNP-Experimente verwendet werden.

**Spin Gunn Effekt**

Die unterschiedliche Elektronenbeweglichkeit in den Minima des Leitungsbandes (lower valley) und dem ersten höheren Subbandes (upper band) ist die Ursache für normalen Gunn Effekt in einigen Halbleitern mit direkter Bandlücke, wie beispielsweise GaAs und InP. In vielen Halbleitern ist die Elektronenbeweglichkeit aber spinabhängig. Deshalb ist zu erwarten, dass eine kleine Spinpolarisation (hervorgerufen durch eine thermische Fluktuation oder durch Spin-Bahn Effekte) anwächst und zu spinpolarisierten Domänen führt. Dies bezeichnet man als den “Spin Gunn Effekt”.

Innerhalb einer Spin Gunn Domäne wird das Elektronenspin-System aus seinem Gleichgewichtszustand gebracht und zeigt die Tendenz, zurück in den Grundzustand zu relaxieren. In einer Situation, in der die Elektronen stark an die Kerne gekoppelt sind, wird erwartet, dass der Übergang des Elektronenspin-Systems in den thermischen Grundzustand dazu führt, die Kernspins auf dynamische Art und Weise zu polarisieren. Um den Effekt spinpolarisierter Domänen auf die Polarisation der Kernspins zu untersuchen, führten wir bei angelegten DC Pulsen herkömmliche NMR Messungen an GaAs und InP Wafern mit unterschiedlichen Dotierungen durch.


Ausgehend von unserer Untersuchungen möglicher Spin Gunn Effekte in InP und GaAs folgen wir, dass es aufgrund der hohen elektrischen Leitfähigkeit nicht möglich ist, den Gunn Bereich in metallischen Volumen-Proben zu erreichen. Dünne epitaxiale Schichten mit einer möglichst kleinen Fläche sind deshalb eine grundlegende Voraussetzung für diese Untersuchungen. Unter den experimentellen Bedingungen unserer Untersuchungen scheinen die Elektronenspinpolarisation und die resultierenden DNP - Effekte viel zu klein zu sein um sie innerhalb der Empfindlichkeitsgrenzen der NMR erfassen zu können. Lokale Messtechniken wie zum Beispiel die Faraday Rotation, optisch verstärkte und detektierte NMR and der magneto-optische Kerr Effekt sind besser
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<tr>
<td>2DES</td>
<td>2 Dimensional Electron System</td>
</tr>
<tr>
<td>BIA</td>
<td>Bulk Inversion Asymmetry</td>
</tr>
<tr>
<td>BIP</td>
<td>Bir, Aronov, and Pikus</td>
</tr>
<tr>
<td>CESR</td>
<td>Conduction Electron Spin Resonance</td>
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<tr>
<td>CISP</td>
<td>Current-Induced Spin Polarization</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
</tr>
<tr>
<td>DNP</td>
<td>Dynamic Nuclear Polarization</td>
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<tr>
<td>DP</td>
<td>D’yakonov and Perel</td>
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<tr>
<td>EMT</td>
<td>Effective Mass Theory</td>
</tr>
<tr>
<td>ENDOR</td>
<td>Electron-Nuclear Double Resonance</td>
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<tr>
<td>EPR</td>
<td>Electron Paramagnetic Resonance</td>
</tr>
<tr>
<td>EY</td>
<td>Elliot Yafet</td>
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<tr>
<td>fcc</td>
<td>Face Centred Cubic</td>
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<tr>
<td>FID</td>
<td>Free Induction Decay</td>
</tr>
<tr>
<td>FLASH</td>
<td>Fast Low Angle Shots</td>
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<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
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<tr>
<td>GaAs</td>
<td>Gallium Arsenide</td>
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<tr>
<td>HFI</td>
<td>Hyperfine Interaction</td>
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<tr>
<td>InP</td>
<td>Indium Phosphide</td>
</tr>
<tr>
<td>LEC</td>
<td>Liquid Encapsulated Czochralski</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular Beam Epitaxy</td>
</tr>
<tr>
<td>MIT</td>
<td>Metal-Insulator Transition</td>
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<tr>
<td>MRI</td>
<td>Magnetic Resonance Imaging</td>
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<tr>
<td>NDR</td>
<td>Negative Differential Resistance</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
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<tr>
<td>NTD</td>
<td>Neutron Transmutation Doping</td>
</tr>
<tr>
<td>OPNMR</td>
<td>Optically-Pumped Nuclear Magnetic Resonance</td>
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<tr>
<td>PM</td>
<td>Paramagnetic</td>
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<tr>
<td>ppm</td>
<td>Parts per million</td>
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<tr>
<td>QW</td>
<td>Quantum Well</td>
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<tr>
<td>RF</td>
<td>Radio Frequency</td>
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<td>SHE</td>
<td>Spin Hall Effect</td>
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<td>Semi-Insulating</td>
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