OPTICAL STUDIES AND BIOLOGICAL APPLICATIONS OF SPINS IN SEMICONDUCTORS

DISSERTATION

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By

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ABSTRACT

Control of electronic spins in paramagnetic systems opens new avenues for the next generation of logic and memory devices. It also gives us new opportunities in biomedical applications such as nano-MRI. Polarization of spins in optically-active paramagnetic materials, such as gallium arsenide (GaAs), is achieved by optical pumping and the system can be manipulated using an external magnetic field or microwave radiation. The status of these spins is detected by measurement of photoluminescence. Specifically, the spin relaxation time of bulk and membrane GaAs were studied via the Hanle effect, in which spins are made to precess by a perpendicular external field. This work laid a foundation for developing a material non-specific spin detection technique for paramagnetic materials, like silicon, which combines optical detection with magnetic scanned probe. Additionally, we studied the multiferroic properties of europium titanate on dysprosium scandate which is a new class of multiferroic material whose properties are controlled by strain engineering. Europium titanate on dysprosium scandate could be used for spintronic applications, such as multiferroic memories in the future using its magnetoelectric coupling. Finally, this thesis focuses on studies of localized electron spins of negatively charged nitrogen-vacancy (NV) centers in diamond using optical detection and their applications to bio-molecular studies. The spins of localized electrons of NV centers can be polarized, manipulated and detected by optically detected magnetic resonance (ODMR) with a high resolution. These unique spin properties can be used to develop highly sensitive vector
magnetometry. This thesis presents the successful development of the scanning vector field magnetometry using the NV centers in diamond and concludes by surveying the possible applications to biological systems.
To Jin, Sean, Dann, Ryan, Parents, and Lord Jesus Christ.
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Chapter 1

Introduction to Spintronics and Optical studies of spin systems

1.1 Quick overview of Spintronics

For last half of the 20th century, there have been great advances in electronics. This advance is most clearly demonstrated in the development of microprocessor technology, which is described by Moore's law. Moore’s law predicts that the number of transistors in a single chip, and therefore, the microprocessor power, will double every 18 months until 2015 or later. This implies that we are going to hit the end of the silicon roadmap, since the size of individual bits is quickly approaching the dimensions of an atom. Another quickly growing problem with current electronic technology is growing power consumption and heat generation. Ever since these fundamental limits of current silicon based technologies were predicted, various new concepts have emerged. One of the most promising technologies is spin electronics (spintronics), a term which describes the field of research on electronics in which electron spin, in addition to charge, is manipulated. Electron spin, often just called ‘spin’, is one of the fundamental properties of an electron as well as its charge. Spin is a pure quantum phenomenon and new logic devices could be made by manipulating the spin state of various systems. A spintronic device will have low power consumption since no flow of charge is required. Processing and memory (or even data storage) on the same chip
could be realized, eliminating the bottleneck problem that current technology is fac-
ing. A spintronic device will be nonvolatile, just like a flash memory. It will operate
at high speed since all it needs is just flipping spins. For example, devices using giant
magnetoresistance (GMR) and tunneling magnetoresistance (TMR) show the great
potential to become promising spintronic devices. First generation spintronic devices
using the giant magnetoresistance (GMR) effect are metal based devices and already
in the market being used as read heads in hard drives. Due to the high impact of this
effect, the 2007 Nobel Prize was awarded to Albert Fert and Peter Grunberg who are
the GMR pioneers.

Another active area of ‘spintronics’ research is based on semiconductor devices.
The fact that semiconductor-based spintronic devices are not only multi-functional,
but also easily integrated with traditional semiconductor technology, makes this area
of research so attractive. In order to make plausible spintronic devices using semicon-
ductors, the three following features are required: (1) spin-polarized electrons must
be coherently injected into semiconductors, (2) the polarization of the electrons must
be maintained and manipulated while the electrons are traveling through the devices
and (3) spins must be detected with high fidelity. The first scheme for a spintronic
device based on the metal-oxide-semiconductor technology was spin field effect tran-
sistor (spin-FET) proposed in 1989 by Datta and Das[1] as shown in Fig.1.1[2]. In
this spin-FET device, a two dimensional electron gas (2DEG) layer is formed between
indium aluminum arsenide (InAlAs) and indium gallium arsenide (InGaAs). One fer-
romagnetic electrode acts as a spin injector and this allows spins to enter the 2DEG
with the same orientation as the magnetization of the ferromagnetic electrode. The
other ferromagnetic electrode serves as a spin detector which accepts spins with the
same orientation as the magnetization of the electrode and filters out everything else.
The gate electrode produces a voltage which is turned into the magnetic field $B_g$, 

due to the relativistic motion of the electron relative to the electric field. This is a spin-orbit (SO) field and \( B_g \) is proportional to \( \nabla V_g \times \mathbf{p} \), where \( V_g \) is the gate voltage and \( \mathbf{p} \) is the linear momentum of the electron. The injected spins from the spin injector precess around this perpendicular magnetic field at the Larmor frequency, 
\[ \omega_L = g_e \mu_B B_g / \hbar, \]
where \( g_e \) is the Landé-g factor of the electron, \( \mu_B \) is the Bohr magneton of the electron and \( \hbar \) is the reduced Plank constant. Thus, spin current at the spin detector is modulated by the degree of precession introduced by the gate field \( B_g \). Electrons pass through the detector if their spins are in parallel, and do not if they are antiparallel with the magnetization of the detector. Additionally, spin information will be lost over time, \( \tau_s \), called the spin lifetime. This is an important parameter. The spin flip length, \( L_s \), is given by \( \sqrt{D_s \tau_s} \) for diffusion regime (in the absence of an electric field) and \( v_d \tau_s \) for drift regime (in the presence of an electric field), where \( D_s \) is the spin diffusion constant and \( v_d \) is the drift velocity. \( L_s \) sets the length scale of spin based devices such as a spin-FET. One of the advantages of using semiconductors for spintronic device is a long spin flip length. Spin flip lengths of several micrometers are possible in semiconductors[3, 4] and this is a great advantage for spin transport. Another class of spintronic device involves the manipulation of spins to exploit their quantum properties in solid-state systems. Here, the ‘spin’ can be an electron spin or a nuclear spin.

Spin properties of materials are not only useful for making spintronic logic and computing devices but also very useful for biological applications. magnetic resonance imaging (MRI) is one of the best examples. MRI is a very powerful tool in medicine and neuroscience, allowing medical technicians to acquire 3 dimensional morphological and functional information. However, it has limited spatial resolution down to 10\( \mu m^3 \) and low field sensitivity. In order to circumvent these problems, researchers have combined MRI techniques with magnetic force microscope (MFM) and thus were
Figure 1.1: The spin-FET proposed by Datta and Das. A ferromagnetic emitter (spin injector) (purple) injects spins (red spheres) into a 2DEG channel (blue), which are manipulated by the gate electrode (gold). The spins are collected by another ferromagnetic collector (spin detector). With the gate voltage off (top), the aligned spins pass through the channel and are collected at the collector. With the gate voltage on (bottom), the field produces a spin-orbit interaction that causes the spins to precess. If the spins are not aligned with magnetization direction of the spin detector after precession of the spins, no current can flow. The figure was taken from Ref.[2]
able to achieve single electron spin measurements[5]. More recently, imaging of the tobacco mosaic virus has been achieved using nuclear magnetic resonance with spatial resolution down to 4nm[6].

1.2 Organization of the dissertation

In Chapter 1, I briefly cover the mechanism of spin relaxation which is important background information for the works presented in this thesis. Then, I introduce different optical techniques to study spin systems. In Chapter 2, I discuss my work on measuring the spin lifetime in gallium arsenide (GaAs). Then I extend the discussion to include the development of a non-material specific spin measurement tool by combining optical techniques with force measurement techniques. In chapter 3, I discuss the magnetic properties of a multiferroic europium titanate thin film. This is a new class of material in which the multiferroic properties are controlled by strain engineering and that could possibly be used for electric field controlled spintronic devices in the future. In Chapter 4 to 6, I focus on developing magnetometry using electronic spins in nitrogen-vacancy (NV) centers in diamond. In Chapter 4 I provide the background physics of NV centers in diamond and Chapter 5 demonstrates the development of scanning vector field magnetometry using the NV centers in bulk-diamond. I discuss possible biological applications using NV centers in nanodiamond in Chapter 6. I mainly focus on studying dynamics of DNA and vector field imaging of magnetotactic bacteria using NV centers in nanodiamond.
1.3 Spin relaxation mechanism

1.3.1 $T_1$ and $T_2$

There are two primary ways to lose spin information. When spins lose energy to the surrounding thermal bath (the lattice) and relax to thermal equilibrium, it is characterized by time constant $T_1$. $T_1$ is the time it takes for the longitudinal (parallel to an external field) magnetization to reach equilibrium and is called the spin-lattice relaxation time. On the other hand, when spin coherence is lost in the transverse (perpendicular to an external field) direction due to spatial and temporal fluctuations of the precession frequency of each spin, it is characterized by time constant $T_2$. $T_2$ is called the spin dephasing time. Spin-lattice relaxation and spin dephasing are usually defined by the Bloch-Torrey equations[7, 8]. The Bloch equations, which are phenomenological, describe the dynamics of electron spin or magnetization and Torrey later generalized the Bloch equations by adding an additional term to explain the transfer of magnetization (spin) by diffusion.

$$\frac{\partial M_x}{\partial t} = \gamma (M \times B)_x - \frac{M_x}{T_2} + D\nabla^2 M_x, \quad (1.1a)$$

$$\frac{\partial M_y}{\partial t} = \gamma (M \times B)_y - \frac{M_y}{T_2} + D\nabla^2 M_y, \quad (1.1b)$$

$$\frac{\partial M_z}{\partial t} = \gamma (M \times B)_z - \frac{M_z - M_0^0}{T_1} + D\nabla^2 M_z. \quad (1.1c)$$

Here $\gamma = \mu_B g / h$ is the electron gyromagnetic ratio in a sample, $D$ is the diffusion constant and $M_0^0$ is the thermal equilibrium magnetization. Spatial inhomogeneity of an external field plays an important role and is often observed to affect $T_2$. To describe such reversible phase losses, which could be recovered by spin-echo experiments, $T_2^*$ is used to describe spin dephasing of ensemble spins, while $T_2$ is reserved for irreversible loss of the ensemble spin phase. In general, $T_2^* < T_2$ for local electrons and $T_2^* \approx T_2$ for conduction electrons since spatial inhomogeneity of an external field is inhibited.
by *motional narrowing* due to the itinerant nature of conduction electrons. Another thing to point out is the relation between $T_1$ and $T_2$. The inequality $T_2 \leq 2T_1$ always holds true[9], however, in most cases, $T_1$ is greater than $T_2$. Measurement techniques for these timescales can be categorized in two groups. Magnetic resonance is used to measure these time scales for localized electrons. For conduction electrons, the Hanle effect, or time resolved pump-probe experiments are generally used. Both the Hanle effect and electron spin resonance will be explained in more detail in Chapter 2 and Chapter 4, respectively.

### 1.3.2 Spin relaxation mechanism of conduction electrons

Four mechanisms have been found to explain the spin relaxation of conduction electrons in metals and semiconductors.

**Elliott-Yafet mechanism** Conduction electron spins can relax via ordinary momentum scattering if there is a spin-orbit coupling induced by an electric potential from the lattice and impurities. Eq.1.2[9] shows that this is usually more important for small band-gap semiconductors and large spin-orbit coupling. This is also the dominant spin relaxation mechanism for metals and small band-gap semiconductors with inversion symmetric structure (e.g. silicon). As shown in Eq.1.2, the spin relaxation time is proportional to the momentum scattering time in this case.

$$\frac{1}{\tau_s(E_k)} = A \left(\frac{\Delta_{SO}}{E_g + \Delta_{SO}}\right)^2 \left(\frac{E_k}{E_g}\right)^2 \frac{1}{\tau_p(E_k)}$$

where $\tau_p(E_k)$ is the momentum scattering time at energy $E_k$, $E_g$ is the energy bandgap, and $\Delta_{SO}$ is the spin-orbit splitting of the valence band.

**D’yakonov-Perel’ mechanism** This occurs in structures lacking inversion symmetry, where the consequent electric field can result in appreciable spin-orbit fields.
Inversion asymmetry can be inherent to the material (for e.g. GaAs), or due to the device being a heterostructure, or under strain. Spin lifetime in this case is inversely proportional to the momentum scattering time.

\[
\frac{1}{\tau_s} \propto \tau_p
\]  

(1.3)

**Bir-Aronov-Pikus mechanism** The exchange interaction between holes and electrons results in an effective magnetic field which leads to inhomogeneous dephasing. This is the dominant spin relaxation mechanism in p-doped semiconductors.

**Hyperfine interaction mechanism** The hyperfine interaction is the magnetic interaction between electron spins and nuclear spins. It is well known that the hyperfine interaction is an important mechanism for spin-spin decoherence of localized electrons. It is usually not an important mechanism for free electrons in metals or in bulk semiconductors above the metal-insulator (MI) transition as spatial inhomogeneities of hyperfine fields are inhibited by motional narrowing due to the itinerant nature of electrons[9]. However, it becomes a more significant mechanism for localized electrons, which are confined in quantum dots or bound on donors and defects. This is a dominant spin relaxation mechanism for GaAs below the MI transition or Nitrogen-Vacancy centers in diamond. This will be discussed more in Sec.4.5.2.

### 1.4 Optical studies of spin systems

There are several different techniques to measure spin systems of conduction or localized electrons. Among these, optical techniques are one of the most powerful for studying spin dynamics of conduction and localized electrons. Here, I focus on spin
polarization using laser radiation and spin detection by using a laser as a probe or by measuring photoluminescence.

1.4.1 Motivation

Optical measurements of spin systems have many advantages. One of the main advantages is high sensitivity. Several optical techniques are sensitive enough to measure a single spin, which is impossible with methods such as conventional nuclear magnetic resonance (NMR) or electron magnetic resonance (EPR)[10]. Selectivity is another reason to use optical techniques. Often, a laser can be focused down to a diffraction-limited spot size, which is roughly half of the wavelength of the source radiation. For instance, by using a technique called REversible Saturable OpticaL Fluorescence Transitions (RESOLFT)[11], spatial resolution of as low as tens of nanometers can be reached. Laser techniques also offer extremely high temporal resolution, down to femtoseconds or lower[12, 13]. Additionally, spin systems can be excited by light of a certain wavelength and wavelength-dependent spin properties can be measured as well. Speed is another reason to use optical techniques. Magnetic resonance requires that the electron spins populate different spin states in the system, in order that transitions between these states can be induced. In conventional magnetic resonance, this population difference is achieved by thermal relaxation through coupling to the lattice, but this coupling process is too slow at low temperatures for magnetic resonance experiments[14]. However, optical excitation provide rapid polarization of spins and this can be orders of magnitude faster than the thermal polarization process, independent of temperature. If spins in the excited states need to be studied, spins cannot be populated by thermal polarization processes and it may be necessary to use light to populate this state[15].

Laser light can be used to enhance the spin polarization and observe the transitions
between states for conventional EPR or NMR techniques[16]. Conversely, optical
detection can be used without increasing the spin polarization. However, in many
cases, it is advantageous to use both techniques. A single laser beam can be used to
both increase the spin polarization as well as read-out the spin state through detection
of a fluorescence signal emitted by the spin system, as in a nitrogen-vacancy center in
diamond. This optical detection technique is discussed in greater detail in Chapter
4. Additionally, one wavelength laser could be used to polarize the spin states and
then the spins can be probed with a different wavelength laser[17].

1.4.2 Optical polarization of spin systems

There are various ways to achieve spin polarization using light. Here, I discuss four
different ways to polarize spins optically. These four different optical polarization
techniques are summarized in Fig.1.2.

Optical pumping This is one of the best known ways to achieve spin polarization
optically. If a solid state medium is irradiated by circularly polarized light, spin
polarized electrons are pumped to the excited state governed by the selection
rule, $\Delta m_j = \pm 1$. This is a commonly used technique, especially for direct
bandgap semiconductors such as GaAs. This is shown in Fig.1.2(a) and is
discussed more in Chapter 2.

Spin exchange Spin polarization can be transferred between two different spin sys-
tems even across different particles[14]. This is particularly useful in case the
spin system is not optically polarizable. One example is Xe[14]. These atoms
cannot be optically pumped from their electronic ground state but can be polar-
ized by spin exchange: spin is transferred from an alkali gas which is optically
spin polarizable. If these two species form a quasi-molecule through the van der
Waals force, the two spins can be coupled by a dipole-dipole interaction. This
coupling allows simultaneous spin flips of the two species and thus transfers spin polarization from one to another. This is illustrated in Fig.1.2(b).

**Inter-system crossing** In many optically detected magnetic resonance (ODMR) experiments, illumination of light excites the system into the spin triplet excited states. Spins relax to ground spin triplet states via spin singlet metastable states. This is a non-radiative, spin dependent process that leads to spin polarization of the ground spin triplet state. In many cases, this is a very efficient process which achieves high spin polarization even without using polarized light. This is discussed in depth in Chapter 4 in the context of ODMR of Nitrogen-Vacancy centers in diamond.

**Spectral holeburning** In an electric field directed toward a fixed nucleus, the plane of a classical orbit is fixed in space and orbital angular momentum is constant.
However, when unpaired spins are in the outermost shell, they experience an intense inhomogeneous electric field produced by neighboring ions. This inhomogeneous electric field is called the *crystal field* [18]. While total angular momentum states are degenerate in free space, the crystal field lifts this degeneracy. So, the plane of this orbit will move about in a noncentral field. Thus, angular momentum will no longer be a constant but will average to zero. In this case, the orbital angular momentum is said to be quenched. If the angular momentum is quenched, optical pumping with circularly polarized light is no longer possible to polarize electron spins. However, if the different spin states can be distinguished in energy space, the laser can selectively excite a spin state, e.g. spin up, in the ground state. This is denoted as $|g_{↑}\rangle$ in Fig.1.2(d). Since the excited state can decay to both ground spin states, the system ends up being polarized to $|g_{↓}\rangle$. This is known as spectral holeburning.

### 1.4.3 Optical detection of spin systems

**Magneto-Optic effect** When light interacts with magnetic materials, either the change in the polarization or the intensity of light is linearly proportional to the magnetization of the materials. These are called magneto-optic effects. The magneto-optic Kerr effect is a measurement of the reflected light, while the Faraday effect is a measurement of the transmitted light. This is usually applied to ferromagnetic or paramagnetic materials. If the excited states of paramagnetic material are spin polarized by optical pumping, absorption of right- and left-handed circularly polarized light will be proportional to the availability of the states. Thus, a spin population difference results in rotation of linearly polarized light which is a superposition of right- and left-handed circularly polarized light. This is further discussed in Sec.3.4.2.
**Photoluminescence** Measurement of photoluminescence is one of the most commonly used techniques to measure spin polarization. There are mainly two different schemes to measure spin polarization. One is the measurement of spin polarization of excited states for conduction electrons. Often, spin polarization is prepared by the previously described optical pumping method. And, just like optical pumping, spontaneous emission is also governed by selection rules. Thus, the polarization of the spontaneously emitted light depends on the spin states of the excited state. The spin polarization as well as spin lifetime can be measured by the so-called *Hanle effect*. Magnetic field dependent spin polarization with continuous optical pumping is affected by the accumulation of phase by all the spins. The polarization of the photoluminescence decreases if a magnetic field is applied perpendicular to the direction of the spin polarization. The linewidth of a Hanle curve is narrowed if the spin lifetime is long and vice versa. Thus, the Hanle effect is a direct measure of the spin lifetime $T^*_2$. This is discussed in depth in Sec.2.1.

If spins of localized electrons are to be measured, optically detected magnetic resonance (ODMR) is used. Spin polarization is prepared by the inter-system crossing method mentioned in Sec.1.4.2. The number of emitted photons is determined by the spin state of the ground state. If the ground state spin polarization corresponds to the transition through spin dependent non-radiative process, the intensity of photoluminescence is reduced and thus a magnetic resonance transition can be measured. This is discussed further in Sec.4.7.

**Spectral holeburning** After spins are polarized by the spectral holeburning, mentioned in the previous section, a second laser beam can be used to monitor the changes in the populations by sweeping the probe beam frequency around the pump beam frequency. The pump laser changes the population of electrons in
different spin sublevels as the laser frequency matches an electronic transition energy. This results in removing electrons from the initial spin sublevel and accumulated in the other spin sublevel. As the probe beam hits the initial spin sublevel, the absorption of probe beam is reduced due to lack of carriers and it is called as a ‘hole’. On the other hand, as the frequency of the probe beam matches with the state where the spins have accumulated, an increase in absorption of the probe beam is observed and this is referred to as an ‘antihole’ as illustrated in Fig.1.3[14]. The separation between the hole and the antihole corresponds to the difference in energy between two spin sublevels and the hole-burning spectrum measures the magnetic resonance transition frequencies. This technique is also useful to study the electronic structure of many systems.
Chapter 2

Optical spin injection and spin detection in Gallium Arsenide

2.1 Hanle effect

2.1.1 Global Hanle effect

Spin polarized electrons in a sample will precess around an externally applied transverse magnetic field and this results in reduction of spin polarization. This is called the Hanle effect. In the case of the continuous-wave (cw) optical pumping of spins, for instance, and globally integrated detection, the spin component along the propagation direction $\hat{k}$ of emitted light in case of photoluminescence measurement is described by the Lorentzian function. This behavior is due to a combination of the spin precession and spin relaxation. The continuous spin pumping process results in accumulation of spin phase due to the different ages of spins present in the sample. While they precess about the transverse magnetic field, their projection along $\hat{k}$, will depend on their age and the magnetic field strength. Spin dynamics can be described by the differential equation

$$\frac{\partial \mathbf{S}}{\partial t} = G + \gamma \mathbf{B} \times \mathbf{S} - \frac{\mathbf{S}}{\tau_s}$$

(2.1)
where $G$ represents spin pumping, $\gamma = g\mu_B$ is the gyromagnetic ratio of electrons of the sample, $\tau_s$ is the spin lifetime. Here $\gamma B \times S$ term describes precession of spins around the magnetic field $B$ and $S/\tau_s$ is a spin relaxation term. As long as the diameter of the area of detection is much longer than the spin diffusion length for a global Hanle measurement, we do not need to consider a diffusion term here. The integral form of Eq. 2.1 and its solution can be written as follows.

$$S_z = A \int_0^\infty \exp\left(\frac{t}{\tau_s}\right) \cos(\gamma B_\perp t) dt$$  \hspace{1cm} (2.2a)

$$= \frac{A'}{1 + (\gamma \tau_s B_\perp)^2}$$  \hspace{1cm} (2.2b)

where $B_\perp$ is purely the transverse magnetic field. Here we consider a magnetic field which is perpendicular to the direction of spins for simplicity. A typical Hanle effect measurement geometry and Hanle curve is shown in Fig.2.1. The linewidth of the Hanle curve $\Delta B = 1/\gamma \tau_s$ in Fig.2.1(b) is inversely proportional to the spin lifetime $\tau_s$. However, in an optical pumping and photoluminescence detection experiment in a direct bandgap semiconductor (e.g. GaAs), $\Delta B = 1/\gamma \tau_s$ is no longer true. Instead, $\tau_s$ should be replaced with $\tau_{\text{eff}}$ where $\tau_{\text{eff}}$ is the measured lifetime and is determined by spin lifetime $\tau_s$ and carrier lifetime $\tau_J$ with the relation $\tau_{\text{eff}}^{-1} = \tau_s^{-1} + \tau_J^{-1}$. However, if there are plenty of unpolarized electrons available in the conduction band of the semiconductor, the number of the photoexcited spin polarized electrons that recombine with holes will be negligible. Thus, in the low optical pump power regime where the number of photoexcited electrons are much less than the number of unpolarized electrons in the conduction band, $\tau_{\text{eff}} \approx \tau_s$.

### 2.1.2 Local Hanle effect

Now we focus on the case of Hanle response of local spins which were created by Gaussian point injection optically as shown in Fig. 2.2(a). Fig. 2.2(a) is a calculated
Figure 2.1: Global Hanle effect. (a) Typical geometry of Hanle measurement. Injected spins are aligned to $\hat{y}$ axis and precess about $\hat{z}$ axis. (b) Schematic representation of a global Hanle curve.

The spatial profile of $S_z$ which is just the result of point injection and diffusion of spins.

Now we add a spin diffusion term to Eq. 2.1.

$$\frac{\partial S}{\partial t} = G + D_s \nabla^2 S + \gamma B \times S - \frac{S}{\tau_s}$$

(2.3)

where $D_s$ is the spin diffusion constant. We can rewrite Eq.2.3 to the integral form of $S_z$ for 2D.

$$S_z(r) = A \int_0^\infty \frac{1}{4\pi D_st} \exp\left(-\frac{r^2}{4D_st}\right) \exp\left(\frac{t}{\tau_s}\right) \cos(\gamma B_L t) dt$$

(2.4a)

$$= A \text{Re} \left[ 2K \left[ 0, \frac{1}{\tau_s} - i\gamma B_L \right] \right]$$

(2.4b)

where $r$ is the distance from injection point and $S_z(r)$ is the $z$-component of spins at a distance $r$ from injection point. The solution is given by the zeroth of modified Bessel function of the second kind. Note that $(4\pi D_s t)^{-1} \exp(-r^2/4D_st)$ is the solution to the differential equation of just the diffusion term in Eq.2.3 for the 2D case and is
axially symmetric from the injection point of spins. Eq. 2.4b should reduce to Eq. 2.2b by integrating in space:

$$S_z = A \int_0^\infty \left[ \int_0^\infty \frac{1}{4\pi D_s t} \exp\left(-\frac{r^2}{4D_s t}\right) 2\pi r dr \right] \exp\left(-\frac{t}{\tau_s}\right) \cos(\gamma B_\perp t) dt \quad (2.5a)$$

$$= \frac{A'}{1 + (\gamma \tau_s B_\perp)^2} \quad (2.5b)$$

Here, $(4\pi D_s t)^{-1} \exp(-r^2/4D_s t)$ is the probability of finding the $z$-component of spins at a distance $r$ and must be unity if integrated over all space. Fig. 2.2(b) contains plots of $S_z(r, t)$ which considers the spin diffusion term and the spin relaxation term only. In other words, this is the $z$-component of the spin density at various distances in the absence of a magnetic field.

$$S_z(r, t) = \frac{1}{4\pi D_s t} \exp\left(-\frac{r^2}{4D_s t}\right) \exp\left(-\frac{t}{\tau_s}\right) \quad (2.6)$$

At $r = 0.25L_s$, the probability density of spins of age has a very narrow distribution function in time and therefore the majority of spins in the sample are fresh (recently injected). It is clear that it requires very high field to reduce $S_z$ for the case of $r = 0.25L_s$ due to the fact that $\omega = \gamma B_\perp$. This results in a very broad Hanle curve compared to the global Hanle curve as shown in Fig. 2.2(d). Fig. 2.2(d) contains computed Hanle curves by analytically solving Eq. 2.2b for global Hanle and Eq. 2.4b for local Hanle effects. The global Hanle curve (black) is a Lorentzian function as discussed in the previous section. The local Hanle curve near the injection point (blue) is no longer Lorentzian. However, as the detection spot gets further away, the distribution function of $S_z$ gets broader and peak position in time moves away from zero. This means that spins far away from the injection point are older and can have many different phases. Depending on the strength of the transverse magnetic field, the sign of $S_z$ can even be negative and this is shown in Fig. 2.2(c). Spins at $r = 3L_s$ have a distribution in time as shown by the purple curve in the absence of
the transverse magnetic field. If transverse magnetic field with magnitude $\gamma \tau_s B_\perp = 2$
is applied, spins precess at the rate of $2/\tau_s$ and this is shown by the magenta curve.
Since a majority of spins have precessed through an angle of $\pi/2$, a negative lobe
appears in the Hanle measurement as shown in Fig.2.2(d).

2.2 Optical spin injection

2.2.1 Electronic band structure of Gallium Arsenide

Gallium arsenide (GaAs) is one of the typical examples of zinc blende structure. It
has a face centered cubic (FCC) structure with a basis consisting of two different
atoms at $(0,0,0)$ and $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. In contrast, silicon or germanium have a diamond
structure which has a fcc lattice with a basis at $(0,0,0)$ only. One can easily see that
it lacks inversion symmetry which is an important factor in some applications. Here,
we only focus near the Brillouin zone center $\Gamma(\mathbf{k} = 0)$ since most optical transitions
takes place near the zone center. The characteristics of the conduction band and the
valence band are s-like($L = 0$) and p-like($L = 1$) near the zone center, respectively.
Away from the zone center, however, these s and p states are not eigenstates anymore.
Some s and p characteristics are mixed in the conduction band and the valence band.
Thus, band structure is no longer parabolic away from the zone center.

Total angular momentum near the zone center of the conduction band is $J = 1/2$
due to the fact that $L = 0$ and $S = 1/2$. However, the situation in the valence
band is a little more complicated because $L = 1$ and $S = 1/2$. There is significant
spin-orbit interaction and $L$ and $S$ are no longer good quantum numbers. Therefore,
total angular momentum $J$ and $J_z$ should be considered. It becomes obvious that the
valence band has six subbands with $(J, J_z) = (\frac{3}{2}, \pm \frac{3}{2}), (\frac{3}{2}, \pm \frac{1}{2}), (\frac{1}{2}, \pm \frac{1}{2})$. Four $J = 3/2$
subbands are degenerate whereas, two $J = 1/2$ subbands are split from $J = 3/2$ by the
spin-orbit interaction energy $\Delta_{SO}$. $(J, J_z) = (\frac{3}{2}, \pm \frac{3}{2}), (\frac{3}{2}, \pm \frac{1}{2})$ bands are degenerate at
Figure 2.2: Local Hanle effect in 2D. (a) The spatial map of $S_z$ pumped by point injection optically. Spin diffusion and Gaussian shape point injection is considered with the assumption of injection point being much smaller than spin diffusion length $L_s$. $x$ and $y$ axes are normalized by $L_s$. (b) Plots of $S_z(r, t) = (4\pi D_s t)^{-1} \exp(-r^2/4D_s t) \exp(-t/\tau_s)$ at various distances. Graphs for $r = 1L_s$, $3L_s$ and $5L_s$ are multiplied by 10, 100 and 1000, respectively, for better visibility. (c) Plots of $S_z(t)$ at $\gamma \tau_s B_\perp = 2$ and $r = 3L_s$ with and without precession term. (d) Analytical solutions of integrated $S_z(t)$ over time at various distances. The black curve shows global Hanle effect by integrating $S_z(r, t)$ in all space and time and curves with the rest of the colors are local Hanle effects at various distances.
the zone center but have different curvature (different effective mass). The broadest subbands are called heavy holes while the others are light holes. The irreducible representation is $\Gamma_6$ for the conduction band, $\Gamma_7$ for the split-off valence band and $\Gamma_8$ for the heavy and light hole valence band. The band structure diagram of GaAs is summarized in Fig.2.3. The valence electrons in the two atoms that are shared to form the band structure of the bulk crystal are Ga : $4s^23p^1$ and As : $4s^23p^3$. From considerations of electronegativity, one could see that the valence band is driven by filling the $3p$ orbitals provided by As atoms while the conduction band is more influenced by the loss of $4s$ electrons from the Ga atoms. Thus, the atoms form $sp^3$ hybridization.

Calculation of the dipole transition probability driven by an incident electromagnetic wave requires the knowledge of electron wavefunctions in the conduction and
valence band. The electron wavefunction in the conduction band is described by the Bloch function \[ \Psi_{m_j}^c = \exp(i\mathbf{k} \cdot \mathbf{r}) u_{m_j}(\mathbf{r}) \] (2.7)

Here \( m_j \) represents the projection for the total angular momentum, \( \mathbf{k} \) is the electron wavevector and Bloch amplitude \( u_{m_j} \) is invariant under the symmetry transformation of the crystal \( (u_{m_j}(\mathbf{r}) = u_{m_j}(\mathbf{r} + \mathbf{T})) \). Considering the angular part of the Bloch amplitude, it can easily be separated into orbital and spin parts since \( L = 0 \) and written in the basis of \( |l, m_l, s, m_s\rangle \)

\[
 u_{\uparrow\downarrow}(\mathbf{r}) = S \uparrow \propto |0,0,\frac{1}{2},\frac{1}{2}\rangle, \quad u_{\downarrow\downarrow}(\mathbf{r}) = S \downarrow \propto |0,0,\frac{1}{2},-\frac{1}{2}\rangle
\] (2.8)

Heavy holes and light hole wavefunctions in the valence band are given as follows.

\[
 \Psi_{M\mathbf{k}}^{(hh, lh)} = \exp(i\mathbf{k} \cdot \mathbf{r}) \sum_{m_j} \chi_{Mm_j}(\mathbf{k}) u_{m_j}^{(3/2)} = \exp(i\mathbf{k} \cdot \mathbf{r}) \sum_{m_j} D_{m_j M}^{(3/2)}(\phi, \theta, \psi) u_{m_j}^{(3/2)}
\] (2.9)

where index \( M \) denotes the value of the component of the electron angular momentum in the valence band along the direction of the wave vector \( \mathbf{k} \) and \( M = \pm 3/2 \) for the heavy-hole band (hh), \( \pm 1/2 \) for the light-hole band (lh). \( \chi_{Mm_j}(\mathbf{k}) \) is the coefficient that depends only on the direction of \( \mathbf{k} \) and \( D_{\mu M}^{(3/2)}(\phi, \theta, \psi) \) is the rotation matrices where \( \theta \) and \( \phi \) are the polar angles of vector \( \mathbf{k} \) with respect to some fixed coordinate frame, and \( \psi \) is an arbitrary angle defining the phase of the wave function. Likewise, the electron wavefunction in the split-off band can be described as follows.

\[
 \Psi_{M\mathbf{k}}^{(so)} = \exp(i\mathbf{k} \cdot \mathbf{r}) \sum_{m_j} D_{m_j M}^{(1/2)}(\phi, \theta, \psi) u_{m_j}^{(1/2)}
\] (2.10)

where \( M = \pm 1/2 \) and index \( m_j = \pm 1/2 \).

The Bloch amplitude \( u_{m_j}^j = |j, m_j\rangle \) can be expressed in the basis of \( |l, m_l, s, m_s\rangle \) by Clebsch-Gordon coefficients or by using the raising and lowering operators \( J_{\pm}\langle j, m| = \)
\( h[(j \mp m)(j \pm m + 1)]^{1/2}|j, m \pm 1\rangle \) for \( j = 3/2 \) as follows.

\[
w_{m_j}^j = |j, m_j\rangle
\]

\[
\begin{align*}
|\frac{3}{2}, \frac{3}{2}\rangle &= |1, 1, \frac{1}{2}, \frac{1}{2}\rangle \\
|\frac{3}{2}, -\frac{1}{2}\rangle &= \frac{1}{\sqrt{3}}(|1, 1, \frac{1}{2}, \frac{1}{2}) + \sqrt{2}|1, 0, \frac{1}{2}, -\frac{1}{2}\rangle \\
|\frac{3}{2}, \frac{1}{2}\rangle &= \frac{1}{\sqrt{3}}(|1, -1, \frac{1}{2}, \frac{1}{2}) + \sqrt{2}|0, 0, \frac{1}{2}, 0\rangle
\end{align*}
\]

\[
\text{hh (lh) for } m_j = \frac{3}{2}
\]

\[
|\frac{1}{2}, \frac{1}{2}\rangle = \frac{1}{\sqrt{3}}(|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) - |1, 0, \frac{1}{2}, \frac{1}{2}\rangle \\
|\frac{1}{2}, -\frac{1}{2}\rangle = -\frac{1}{\sqrt{3}}(|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) + |1, 0, \frac{1}{2}, \frac{1}{2}\rangle
\]

\[
\text{split-off hole}
\]

(2.11)

### 2.2.2 Spin-polarized excitation and detection with circularly polarized light

Now we consider optical excitation over the bandgap of the semiconductor by optical radiation. By Fermi’s golden rule, the probability of transition between valence band and conduction band by optical excitation with photon energy \( h\omega \) is

\[
R_{vb \rightarrow cb} = \frac{2\pi}{\hbar} |\langle \Psi_{cb} | -\mu_e \cdot E | \Psi_{vb} \rangle|^2 \delta(E_g - h\omega) \quad (2.12)
\]

where electric dipole moment \( \mu_e = -er \), \( e \) is the charge of electron, \( r \) is the displacement vector pointing from the negative charge to the positive charge, and \( E \) is the electric field of the optical radiation. Here we evaluate \( -\mu_e \cdot E \) for circularly polarized light.

\[
E(r, t) = E_0(e^{i(k \cdot r - \omega t)} \hat{x} + e^{\pm i\frac{\pi}{2}} e^{i(k \cdot r - \omega t)} \hat{y} = E_0 e^{i(k \cdot r - \omega t)}(\hat{x} \pm i\hat{y}) \quad (2.13)
\]

where \( k = k\hat{z} \). Therefore,

\[
-\mu_e \cdot E = -er \cdot E = -erE_0(\sin \theta \cos \phi \hat{x} + \sin \theta \sin \phi \hat{y} + \cos \theta \hat{z}) \cdot (\hat{x} \pm i\hat{y}) = \pm eE_0Y^\pm_1
\]

(2.14)
Right-handed circularly polarized (RCP) light is represented by $Y_1^{+1}$ and left-handed circularly polarized (LCP) light by $Y_1^{-1}$. Here are the most commonly used expressions of spherical harmonics in this section

\[
Y_0^0 = |0, 0\rangle = \frac{1}{\sqrt{4\pi}}
\]

(2.15a)

\[
Y_1^{\pm 1} = |1, \pm 1\rangle = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}
\]

(2.15b)

\[
Y_0^1 = |1, 0\rangle = \sqrt{\frac{3}{4\pi}} \cos \theta
\]

(2.15c)

Using the following relations we can calculate the transition probabilities with circularly polarized light from the valence band to the conduction band

\[
\sin \theta e^{\pm i\phi} Y_l^m = \pm \left[ \frac{(l \pm m + 1)(l \pm m + 2)}{(2l + 1)(2l + 3)} \right]^{1/2} Y_{l+1}^{m\pm 1} \mp \left[ \frac{(l \mp m)(l \mp m - 1)}{(2l - 1)(2l + 1)} \right]^{1/2} Y_{l-1}^{m\mp 1}
\]

(2.16)

\[
\langle s_1, m_{s_1}|s, m_s\rangle = \delta_{s_1,s}\delta_{m_{s_1},m_s}
\]

(2.17)

\[
\langle l_1, m_1|l, m\rangle = \delta_{l_1,l}\delta_{m_1,m}
\]

(2.18)

and

\[
\int_0^{2\pi} \exp(2i\phi)d\phi = 0
\]

(2.19)

Following are the results for RCP light (Eq.2.20a and 2.20b) and for LCP light (Eq.2.20c and 2.20d) with non-zero transition probabilities.

\[
\left| \left\langle \frac{1}{2}, \frac{1}{2}|Y_1^1\frac{3}{2}, -\frac{1}{2}\right\rangle \right|^2 = \left| \left\langle 0, 0, \frac{1}{2}, \frac{1}{2}|Y_1^1\left(\frac{1}{\sqrt{3}}|1, -1, \frac{1}{2}, \frac{1}{2}\rangle + \sqrt{2}|1, 0, \frac{1}{2}, -\frac{1}{2}\rangle\right) \right\rangle \right|^2 = \frac{C^2}{3}
\]

(2.20a)

\[
\left| \left\langle \frac{1}{2}, -\frac{1}{2}|Y_1^1\frac{3}{2}, -\frac{3}{2}\right\rangle \right|^2 = \left| \left\langle 0, 0, \frac{1}{2}, -\frac{1}{2}|Y_1^1|1, -1, \frac{1}{2}, -\frac{1}{2}\rangle \right\rangle \right|^2 = C^2
\]

(2.20b)
Conduction band

\[ \sigma^+ \quad 3 \quad \sigma^- \]

Valence band

LH, HH

SO

\( m_j = -1/2 \quad m_j = +1/2 \quad m_j = -3/2 \quad m_j = -1/2 \quad m_j = +1/2 \quad m_j = 3/2 \)

\[ \begin{array}{c}
m_j = -1/2 \\
m_j = +1/2 \\
m_j = -3/2 \\
m_j = -1/2 \\
m_j = +1/2 \\
m_j = 3/2 \\
\end{array} \]

Figure 2.4: Optically allowed transitions from the valence band to the conduction band of GaAs near the zone center. Red and blue arrows indicate right- and left-handed circularly polarized light and the thickness of the arrow implies the strength of the transition. Number indicates the ratio between transitions.

\[ \left| \left\langle \frac{1}{2}, \frac{1}{2} \left| Y_1^{-1} \right| \frac{3}{2}, \frac{3}{2} \right\rangle \right|^2 = \left| \left\langle 0, 0, \frac{1}{2}, \frac{1}{2} \left| Y_1^{-1} \right| 1, 1, \frac{1}{2}, \frac{1}{2} \right\rangle \right|^2 = C^2 \quad (2.20c) \]

\[ \left| \left\langle \frac{1}{2}, -\frac{1}{2} \left| Y_1^{-1} \right| \frac{3}{2}, \frac{3}{2} \right\rangle \right|^2 = \left| \left\langle 0, 0, \frac{1}{2}, -\frac{1}{2} \left| Y_1^{-1} \left( \frac{1}{\sqrt{3}} \right| 1, 1, \frac{1}{2}, -\frac{1}{2} \right) + \sqrt{2} \left| 1, 0, \frac{1}{2}, \frac{1}{2} \right) \right\rangle \right|^2 = \frac{C^2}{3} \quad (2.20d) \]

where \( C \) is a constant that is common throughout the non-zero transition equations.

Optically allowed transitions shown above are summarized in Fig.2.4. As one can see, excitation by purely circularly polarized light from only heavy-hole and light-hole valence band will produce \((3 - 1)/(3 + 1) = 50\%\) spin polarization. One can compute the probability of transitions from the split off bands as well.

\[ \left| \left\langle \frac{1}{2}, \frac{1}{2} \left| Y_1 \right| \frac{1}{2}, \frac{1}{2} \right\rangle \right|^2 = \left| \left\langle 0, 0, \frac{1}{2}, \frac{1}{2} \left| Y_1 \left( -\sqrt{\frac{2}{3}} \right| 1, 1, \frac{1}{2}, -\frac{1}{2} \right) + \sqrt{2} \left| 1, 0, \frac{1}{2}, -\frac{1}{2} \right) \right\rangle \right|^2 = \frac{2C^2}{3} \quad (2.21a) \]
\[
\left| \langle \frac{1}{2}, -\frac{1}{2} | Y^{-1}_1 | \frac{1}{2}, \frac{1}{2} \rangle \right|^2 = \left| \langle 0, 0, \frac{1}{2}, -\frac{1}{2} | Y^{-1}_1 \left( \frac{\sqrt{2}}{3} | 1, \frac{1}{2}, -\frac{1}{2} \rangle - | 1, 0, \frac{1}{2}, \frac{1}{2} \rangle \right) \right|^2 = \frac{2C^2}{3}.
\]

As shown in the Eq. 2.21a and 2.21b, the split-off bands are excited too, along with the LH and HH bands. If the laser wavelength is set to cover the split-off bands as well, the overall probability of transition to both the spin states would be equal and no spin polarization will be obtained. Thus, it is important to tune the excitation laser wavelength properly to exclude the split-off bands to polarize spins in the conduction bands.

Conversely, polarized spins could be measured by recombination process. When the electrons recombine with holes, the same selection rules apply. This is simply the inverse of the optical excitation. For bulk GaAs, the maximum optical polarization is only 50% even when electron spins are 100% polarized when the wavelength of the measured photoluminescence is tuned to the bandgap. This is again due to the degeneracy of heavy-hole and light-hole valence band. Therefore, optical polarization can go only up to 25%, if spins are pumped optically and detected by spin-PL detection. In case of quantum well (QW) structures, optical polarization can go up to 100% which corresponds to 100% spin polarization due to the fact that the degeneracy of heavy-hole and light-hole band is lifted.

### 2.3 Spin-PL measurement in GaAs

An experiment was designed to establish optical injection and detection of spins in GaAs in conjunction with detection techniques using magnetic force microscopy. The nature of spins in direct bandgap materials have been well studied using optical techniques such as spin-dependent photoluminescence[20], spin-polarized electrolumines-
cence [21, 22], and magneto-optic effect [4, 23–25]. The main drawback of these techniques, however, is that they work only for optically active materials such as the direct bandgap III-V semiconductors. Electrical detection technique is the only available method to directly characterize spins in optically inactive materials such as silicon. The main trouble with the electrical detection technique is that the ferromagnet-semiconductor interfaces introduce a large degree of complexity to spin-dependent behavior. Thus, there has been a need to develop a material non-specific imaging and spectroscopic tool to characterize spins in semiconductors. Using magnetic force microscopy by direct magnetic dipolar coupling to the electron spins in semiconductors becomes a very attractive approach in the sense that it is material and/or structure insensitive. Thus, this can be used for studying spins in optically inactive materials such as silicon and graphene which are very appealing materials for spintronic applications due to the expected long spin lifetime given by small spin-orbit coupling and integrability to current semiconducting industry. However, the development of such a tool is very challenging for several reasons. One is that the extremely small number of non-equilibrium spins injected in these paramagnetic materials results in extremely small magnetic forces. Second is that magnetic field produced by the tip perturbs spins in the paramagnetic materials. Thus, it is essential to understand inhomogeneous field effects on spins. This brings us first to establish optical studies of spins in GaAs so that we can understand spins well without such perturbation. Then we can apply the magnetic force microscopy technique to understand spin dynamics in such an environment. Spin dependent photoluminescence is used to measure spin properties in GaAs for such studies.
2.3.1 Spin dynamics on bulk epitaxial GaAs

Sample preparation

The 2µm thick n-GaAs (100) layer with doping level of $3 \times 10^{16} \text{cm}^{-3}$ was epitaxially grown using molecular beam epitaxy (MBE) system. The doping level, which is just above the metal-insulator (MI) transition, was chosen to have maximum spin lifetime[20]. The growth structure is shown in Fig.2.5. A sacrificial layer of AlGaAs was grown to facilitate back etching of the wafers to make GaAs membrane region for magnetic force microscope (MFM) studies and the this is discussed in Section 2.3.2.

Experimental setup

The details of an experimental setup to measure spin dependent photoluminescence (spin-PL) from bulk GaAs are as follows. A cw-laser beam from Ti:sapphire laser (Mira, Coherent) was used as a pump beam to optically pump spins into the conduc-
tion band of a GaAs sample. The wavelength was tuned to 780nm so that the energy of the pump laser is greater than the bandgap of GaAs (1.52eV at 4K) but small enough to exclude transition from the split-off band to the conduction band to create spin polarization as we discussed in Sect.2.2.2. The pump laser was initially linearly polarized to s-polarization using a Glan-Thompson polarizer and then converted to circularly polarized light by using an electro-optic modulator (EOM) (EO-PM-NR-C1, Thorlabs). The EOM is a voltage controlled waveplate that allows us to produce circularly polarized light. Voltage is modulated to create right- and left-circularly polarized light to measure spin-PL. Fig.2.6 shows that circular polarization of PL from GaAs is fully modulated by changing the offset voltage of EOM through which the pump beam passes. After the polarization of the pump beam is modulated by the EOM, laser beam is focused onto GaAs sample which is mounted on an optical flow cryostat (ST-300, Janis Research) using a doublet achromatic lens. Due to the low numerical aperture of the given optics, the focused laser spot size is estimated to be 30µm or larger which is much longer than the spin diffusion length. Thus, our measurement is not expected to observe spin diffusion effects. Sample is cooled to 17K during the measurement. Circularly polarized PL emitted from the sample is collimated using a doublet achromatic lens and converted to linear polarization using a zeroth order half waveplate and then the polarization is analyzed by another polarizer before a spectrometer with LN cooled CCD (Spec-10:256 / ST133B, Princeton instruments). Transverse magnetic field is applied along the \( \hat{z} \)-direction to measure the Hanle effect. A schematic of the optical setup is shown in Fig.2.7.

**Experimental results from bulk GaAs**

The spectrometer enables us to measure wavelength-resolved spin-PL as shown in Fig.2.8(a). The PL spectrum was taken at 17K and shows two distinct peaks. A
Figure 2.6: Modulation of circular polarization of PL from GaAs. Any degree of circular polarization of pump light is controlled by offset voltage of EOM. EOM offset voltage was calibrated by measuring circular polarization of PL of GaAs in the absence of magnetic field at 17K.

Figure 2.7: Optical setup for measuring spin-PL on bulk GaAs. Direction of transverse magnetic field for Hanle effect is along $\hat{z}$ (out of page). Spin precession direction is denoted by thick green arrow.
peak near 1.49eV corresponds to a donor to acceptor (D-A) transition and a peak at 1.514eV is from transition at the bandedge of GaAs at 17K. The red curve is a PL spectrum for right-handed circularly polarization (RCP). The PL spectrum for LCP (not shown in the Figure) is very similar to the red curve. Circular polarization (blue curve) is the difference between spectra for RCP and LCP divided by the sum. A series of measurement were taken as a function of transverse magnetic field and this is shown in Fig. 2.8(b). Circular polarization shows maximum at 1.52eV. At this point we obtained the best signal-to-noise ratio for Hanle measurement. A Hanle curve obtained at other wavelengths doesn’t look any broader or narrower than the curve at 1.52eV. Thus, the “following” Hanle measurements are thus taken at 1.52eV. Fig. 2.9 shows a pump power dependence measurement. Data was taken by 7.5mW, 4.3mW and 0.9mW pump laser power. As is demonstrated, higher power gives better signal-to-noise ratio. Data was fit to the following equation

\[
S_z = A \int_0^\infty \exp\left(-\frac{t}{\tau_s}\right) \cos(\gamma B_\perp t + \theta)dt \tag{2.22a}
\]

\[
= A' \frac{(\cos \theta - \gamma \sin \theta B_\perp \tau_s)}{1 + \gamma^2 B^2_\perp \tau^2_s} \tag{2.22b}
\]

where \(\theta\) is the angle away from normal incidence of the pump beam. Fit to data for 7.5mW pump laser power gives a spin lifetime \(\tau_s = 88\)ns. This value has a good agreement with literature for a given donor concentration[20].

### 2.3.2 Spin dynamics in epitaxial GaAs membrane

**Sample preparation**

Having established the successful measurement of spin lifetime in bulk GaAs, the next experiment was done on the membrane sample since the membrane sample is used to measure spin dynamics by scanned probe with magnetic tip[26]. In order to create a GaAs membrane device, standard photolithography and wet etching techniques were
Figure 2.8: Spectrally resolved Hanle measurement on bulk GaAs. (a) Photoluminescence (red curve) and circular polarization of light (blue curve) in the absence of magnetic field as a function of photon energy. The peaks at 1.514eV and 1.49eV correspond to the bandedge of GaAs at 17K and a donor to acceptor (D-A) transition, respectively. (b) The dependence of circular polarization of PL as a function of photon energy and transverse magnetic field.
Figure 2.9: Power dependence of Hanle measurement in bulk GaAs. All the curves were taken at 1.52eV. Closed circles are measured values and solid lines are fit to Eq.2.22. Spin lifetime $\tau_s$ was found to be 88ns from fit.

The wafer was back-etched to create large size membranes (0.3mm $\times$ 1mm). The wafers were etched using a mixture of citric acid, hydrogen peroxide and water to allow selective etch between GaAs and AlGaAs. Fig.2.10 shows the image of a back-lit etched membrane. The shape of the membrane is due to the anisotropic nature of the etch along various crystalline directions. A pattern seen on the sample was also etched from the top using hydrofluoric acid to assist with finding the area of interest in a non-optical cryostat using atomic force microscopy. However, since an optical cryostat was used, these patterns do not play any role in the sample except the fact that it was useful for focusing a pump beam on the sample using an objective lens for later experiments.
Figure 2.10: Optical micrograph of a typical membrane sample formed by back etching. The membrane is typically 0.3mm × 1mm. Zoomed-in image shows pump beam from optical fiber transmitted through membrane and the size is measured to be 7µm. Fabrication of the sample was done by G. Xiang.

Experimental setup

The experimental setup for measurement of spin-PL in membrane GaAs is shown in Fig.2.11. An optical fiber was used to pump circularly polarized light into the GaAs membrane sample. This was achieved by carefully inserting a single mode optical fiber into the back-etched hole and gluing it about 15µm away from the back surface of the membrane. The fiber core is 3µm in diameter and allows the injection spot size to be about 7µm. This is comparable to or smaller than the spin diffusion length in GaAs[24]. Photoluminescence is collected from the side to avoid collection of transmitted pump beam. The spectrometer used for the measurement acts as an excellent optical filter and also allows us to measure wavelength-resolved Hanle effect. A bandpass filter with the center wavelength of 820nm and a bandwidth of 10nm was used to ensure complete blockage of all unwanted pump light. Everything else is
Figure 2.11: Optical setup measuring spin-PL on membrane GaAs. An optical fiber was glued about 15\(\mu\)m away from back surface of the membrane GaAs through the back etched hole.

identical to the setup for the bulk GaAs measurement.

Experimental results from GaAs membrane

Fig.2.12(a) shows a Hanle measurement on membrane GaAs with pump power of 33\(\mu\)W with a pump beam size of about 7\(\mu\)m. The solid line is a fit to Eq.2.22b which describes a global Hanle effect. It is quite obvious that the data doesn’t fit Eq.2.22b. Fig.2.12(b) shows a comparison between a Hanle measurement on bulk GaAs (blue) and membrane GaAs (red). Note that the pump beam size for bulk GaAs is about 30\(\mu\)m (\(\gg L_s\)) and is about 7\(\mu\)m (\(< L_s\)) for membrane GaAs. \(L_s \sim 10\mu\)m for GaAs. It is clear that the Hanle curve for membrane GaAs is much broader than the Hanle curve for bulk GaAs. There are two possibilities why the curve from the membrane measurement is so much broader than that of bulk GaAs. One possibility is spin
Figure 2.12: Local Hanle effect on GaAs membrane sample. (a) Hanle measurement on membrane GaAs with pump power of 33\(\mu\text{W}\) (solid circles) and fit using Eq. 2.22b. It shows that the Eq. 2.22b doesn’t fit well to the data and this is due to spin diffusion effect as well as high pump beam power density. (b) Comparison between Hanle measurement of bulk GaAs (blue) and membrane GaAs (red). Pump beam sizes on bulk GaAs and membrane GaAs are about 30\(\mu\text{m}\) and 7\(\mu\text{m}\), respectively. Hanle curve on membrane GaAs is significantly broader than the one from bulk GaAs, yet the percentage of circular polarization is about the same.

diffusion. Due to the fact that spins diffuse out from the detection area which is about the same as pump area (diffusion length of holes are less than a micrometer and the PL detection area is about the same as pump area), the PL measurement only probes fresh spins which are still coherent at high field given the narrow distribution of spins in time as was discussed in Sec. 2.1.2. The other possible cause is high pump power density. As pump power density gets higher, more spin polarized electrons start to recombine with holes. The carrier lifetime begins to play a role in measured lifetime and this makes the Hanle curve broader. In order to separate out these two effects, further measurements were performed.
Spin diffusion effect and pump power density effect on Hanle curve

In order to separate out these two effects, we have used an objective lens (CFI Plan Fluor 10X, Nikon) with numerical aperture of 0.3 and working distance of 16mm. There are several reasons to switch from optical fiber setup to optical setup using the objective lens. Firstly, it requires very careful alignment and gluing to prepare a sample with optical pumping of spins by fiber optics. Secondly, polarization of optics in the optical fiber is very sensitive to the stress applied on the fiber. Since circularly polarized light is prepared and modulated outside of the optical fiber by the EOM, small change of stress on the fiber, which can be induced very easily by just a little bit of bending, causes change in the circular polarization. Since the spin-PL measurement is very sensitive to the degree of circular polarization of the pump beam, controllability of the circular polarization of the pump light is an important factor. Additionally, mechanical vibration of the fiber can cause noise on the spin polarization measurement for the same reason. Lastly, it is impossible to control pump beam spot size with optical fiber setup. Free space setup with an objective lens allows us to control beam spot size independently without changing optical alignment for PL collection.

Another change we made for measurement of spin diffusion effect and pump power density effect is a detection method. All the previous measurements were done using the optical spectrometer with LN cooled CCD. We measured optical polarization by subtracting spectra between right- and left- handed circularly polarized light. This is a DC measurement. If we need to measure at a high speed, this is not an optimal measurement scheme. As we will see in the following section, spin-PL measurement needs to be done at a frequency and phase synchronized with a cantilever motion. A resonance frequency of a cantilever we use is in the range of 6-8kHz. Thus, we need to implement the lock-in detection using a photodiode. Since we know in what
wavelength of PL we need to measure for the spin-PL measurement of GaAs from the previous measurements, we select the spectral range of measurement using the bandpass filter with a center frequency of 820nm and a spectral range of 10nm. In the lock-in detection, we modulate the spin polarization in the GaAs at a driving frequency of the EOM. A lock-in amplifier mixes a signal detected by the photodiode with a reference signal from a frequency source to demodulate the signal. This allows us to measure a signal with a high signal-to-noise ratio by measuring at a high frequency away from the $1/f$ noise and with narrow bandwidth to reject any other unwanted noise including white noise. Before switching to this new measurement scheme, we verified that the lock-in detection method does not affect the spin-signal by comparing a lock-in detected Hanle curve with a Hanle curve measured using the spectrometer. Fig.2.13 shows the same Hanle measurement on the membrane GaAs with two different detectors. The data measured with the spectrometer were integrated over a couple of angstroms of photon wavelengths which is set by the spectral resolution of the spectrometer, while the photodiode’s response is integrated over the 10nm width set by the bandpass filter. This comparison verifies that replacing the spectrometer with lock-in measurement using a photodiode does not make any difference. This is also worth to note that lock-in measurement is used to synchronize with a cantilever frequency for later experiment.

A laser (56RCS-HS, Melles-Griot) beam at $\lambda = 780$nm is initially prepared to s-polarization. An EOM modulates the linearly polarized light at a certain frequency. A pair of lens after the EOM is used to change collimation of the beam in order to control the pump diameter on the sample. Once the collimation of laser is modified, the pump beam is directed into the objective lens using a dichroic mirror (LPD01-785RU-25, Semrock) and focused onto the membrane GaAs sample after it passes through a quarter-waveplate to convert linear polarization of light to circular polarization.
Figure 2.13: Comparison between Hanle measurement using a spectrometer and a lock-in detection with photodiode. Red circles are a measure at $\lambda = 821$nm using a spectrometer. Blue circles are measured at $\lambda = 820$nm with wavelength range of 10nm by a lock-in detection with photodiode. Both signal looks almost identical and the lock-in measurement using the photodiode gives signal-to-noise ratio (SNR) as good as SNR of signal measured by the spectrometer.

Because the linear polarization of light incident on the quarter-waveplate is modulated between two linear states with a phase difference by 180°, the light that falls on the sample is modulated between RCP and LCP. The dichroic mirror is designed to reflect $\lambda = 780$nm and transmit all other wavelengths in order to reject any pump light reflected back from the sample. Photoluminescence from the sample passes through the dichroic mirror and 780nm notch filter (NF03-785E-25, Semrock) to block any unwanted reflected and scattered pump light and is collected by a photodiode (DET110A, Thorlabs). Circularly polarized photoluminescence from the sample is converted to linearly polarized light by the same quarter-waveplate and analyzed by a linear polarizer before the photodiode. A CCD camera was put behind the photodiode so that it can be used to monitor alignment of laser to the sample. In this experiment, lock-in detection is used. A lock-in amplifier (7265, Signal Recovery) demodulates the EOM modulated signal for better signal-to-noise ratio. This setup
Figure 2.14: Schematic diagram of optical setup using an objective lens. This setup is used to separate out diffusion effect and pump beam power density effect. Collimation of the beam is controlled by a pair of lens right after EOM to change the pump beam size on the sample. This was set up by V. P. Bhallamudi and D. Labanowski.

is illustrated in Fig.2.14.

First, a Hanle measurement on GaAs at 10K was performed with a pump size of 30µm with various pump power density. Size of the pump beam was determined by widefield imaging of PL area on the sample using a CCD. Pump size of 30µm is bigger than usual spin diffusion length (∼10µm). Fig.2.15(a) shows Hanle measurements with four different power densities. Circles are data and solid lines are fit to Eq.2.2. It is very clear that all the data are very well fit to Eq.2.2 and this implies that we do not probe any spin diffusion effect here. Additionally, the full-width at half max (FWHM) increases as pump power density increases. Fig2.15(b) shows the FWHM as a function of power density. The FWHM grows linearly with power density. Thus, we can extrapolate to obtain intrinsic spin lifetime which is to remove the effect of carrier lifetime in the spin-PL measurement. The extrapolated FWHM is 5.57G and this corresponds to spin lifetime of 95ns.

Then, the pump beam size was changed down to 10µm and pump power density
Figure 2.15: Hanle measurements with pump beam size of 30µm in various pump power density. (a) Hanle measurements in various pump power densities. The size of the pump beam on the sample is 30µm which was measured by widefield imaging using a CCD camera. (b) The FWHM of the Hanle curves in (a) as a function of pump power density. The FWHMs of the Hanle curves are clearly linear in pump power density and intrinsic spin lifetime found by extrapolation is 95ns. Data were taken by V. P. Bhallamudi and D. Labanowski.
dependence of Hanle measurements was performed. The pump beam size now is comparable to the spin diffusion length and it is expected to see spin diffusion effect. Fig.2.16 shows Hanle measurements with five different pump power densities. Circles are data and solid lines are fit to Eq.2.2. This is quite obvious that data do not fit to the Eq.2.2. This is a strong indication that not only high pump power density affects the linewidth of Hanle curve but also spin diffusion involves here. To separate out spin diffusion effect from pump power density, the data were compared with calculated Hanle curve based on the Hanle measurements with 30µm pump beam size. Hanle curves corresponding to the pump power density used here were plotted based on the findings of the FWHM from Fig.2.15(b). Data with four different pump power density consistently show extra broadening due to the small size of pump beam. Pump size dependent measurements were not performed here but it is expected that
smaller pump beam size will enhance the broadening of the linewidth of Hanle curve by probing smaller subset of spins as we discussed in Sec. 2.1.2.

2.3.3 Local magnetic field effect on spin-PL

Having shown the characteristics of spin signals in bulk and membrane GaAs samples, we now combine magnetic force microscopy with the optical techniques we have discussed so far to develop a material insensitive spin imaging technique. The basic idea is to encode local information in the variation of the global spin polarization in response to a spatially scanned magnetic field from a micromagnetic tip[27]. We still use spin-PL as our detection scheme, which is usually not a suitable measurement technique to get spatially resolved information. As we have seen in the previous sections, coherence of electron spins will be lost at high magnetic field. The magnetic tip does not serve as a probe in this case but it will destroy spin polarization right underneath of the tip due to its high field. It is somewhat analogous to hole burning measurement, which was discussed in Sec. 1.4.3. We can find out local information by removing the spin polarization from the area where we are interested in and measuring global spin signal. Although we are trying to develop this technique in conjunction with optical technique, this in principle can be used with electrical detection[28] as well so that it can measure spins whether the materials are optically active or not. Numerical simulations and extended experiments are presented in Ref.[26]. Here, preliminary result will be shown briefly.

Experimental setup

Optical setup  In order to combine magnetic scanned probe system with optical detection, we have used the same optical setup described in the previous section. The only difference now is that the sample is membrane GaAs and magnetic scanned
Figure 2.17: Comparison of Hanle curves between 30µm and 10µm pump spot sizes. Hanle curves with 10µm pump beam are compared with Hanle curves with 30µm pump beam for four different pump power densities. Circles are data taken with 10µm pump spot size and solid lines are calculated Hanle curve based on the FWHM dependence of pump power density for 30µm pump spot size in Fig.2.15(b).
Figure 2.18: A Schematic diagram of optical setup combined with a micromagnetic tip on a cantilever. The system was set up by V. P. Bhallamudi.

A micromagnetic probe is integrated into the sample area. The EOM is modulated between RCP and LCP at the cantilever resonant frequency \( f_c = 6.8 \text{kHz} \) and the lock-in detection is used to demodulate the signal from measurements with better signal-to-noise ratio and to synchronize with the cantilever oscillation. This is illustrated in Fig. 2.18.

**Micromagnetic probe**  NdFeB spheres were used as micromagnetic probes. The spherical shape is expected to approximate the dipole moment well and NdFeB is a hard-magnet with high coercivity, and can maintain its magnetization even as high transverse field is applied. It also has high magnetization and can thus provide higher dipole field. These particles are carefully glued onto the tip of a micromechanical cantilever under a microscope. The particles were typically glued on silicon nitride triangular cantilevers (spring constant, \( k_0 \sim 0.01 – 0.03 \text{N/m} \)) and epoxy (Stycast1266, Emerson and Cuming) was used to glue the particles because of its well known low temperature properties. The magnetic moment of the sphere was measured to be...
$1.35 \times 10^{-10} \text{J/T}$ using cantilever magnetometry.

**Tip effects on Hanle curve**

Fig.2.19 shows the effect of the magnetic tip on the Hanle response of the GaAs membrane. The green solid line is the Hanle response with the tip far away (about 100µm away), while the other lines are with two positions of the magnetic tip close to the pump, while touching the sample. The Hanle curve without tip effect is mainly determined by spin diffusion effect and high pump power. The Hanle response is seen to be broader when the tip is close to the injection spot. One of the reasons is that the magnetic tip produces a large magnetic field in parallel with spin orientation and in perpendicular to the Hanle field. Thus, the angle between spin orientation and total external field is no longer perpendicular to each other for Hanle measurement that we discussed in previous sections. Instead, there is only a small angle and the angle keeps changing as Hanle field is swept. As well discussed in Ref.[26], this results in broader Hanle curve since the the accumulation of the phase loss is minimized due to small angle of precession. Another possible reason is that spins keep changing their precession angle and frequency as they diffuse out to different regions of the sample given by the magnetic dipolar field. This causes the old spins to lose coherency even at relatively small applied transverse field and hence the Hanle curve becomes broader.

The reason for the asymmetric Hanle curve is possibly due to slight misalignment of the magnetic tip with respect to the optical injection spot. However, extended measurements have to be done in conjunction with theoretical studies.

**2.4 Conclusion**

We have successfully studied spin dynamics in paramagnetic GaAs using optical technique. We have found evidence of local Hanle effect due to the spin diffusion effect.
Figure 2.19: Hanle effect in the presence of a micromagnetic tip. The green solid line shows the Hanle response when the micromagnet is far from the optically spin injected spot. Red and blue dots show the response when the micromagnet is touching the sample and close to the injected spot. Data were taken in collaboration with V. P. Bhallamudi.

We finally demonstrated preliminary results of global spin-PL measurement on spins perturbed by a magnetic scanned probe. This project is actively ongoing and such systems need to be further studied to understand spin dynamics in an environment with inhomogeneous magnetic field. If spin behavior in such an environment is well understood, developing a material non-specific spin imaging tool should be feasible in the future.
Chapter 3
Magnetic properties of multiferroic Europium Titanate

3.1 Introduction

Since spintronics becomes one of the most promising candidate for next generation memory technology due to the fact that it offers low power consumption and non-volatility, this has been a hot topic in condensed-matter research area. Giant magneto-resistance (GMR) read-head in hard drive is successfully commercialized and we all use it on an everyday basis. Magnetic random access memory (MRAM) is another technology that is close to being commercialized. In these devices the magnetization is manipulated with a current-generated magnetic field. This requires high writing energy and there has been possible solutions to reduce writing energy such as using a spin-polarized current to reverse the magnetization by spin-transfer torque rather than using magnetic field. Another possible solution is to use electric field rather than large current. Another reason to control magnetization using electric field is to increase the compatibility with current semiconductor devices. Electric field controlled ferromagnetism has been demonstrated with several different ways such as by controlling magnetostriction produced by strain using piezoelectricity[29, 30], by controlling magnetic anisotropy in ferromagnetic semiconductor, (Ga,Mn)As which depends on the charge carrier concentration[31], or by using multiferroic materials.
By definition, multiferroic material is one that possesses two or three of the so-called ‘ferroic’ properties: ferroelectricity, ferromagnetism and ferroelasticity. The classification of a multiferroic has been broadened to include antiferroic order[32]. Another distinct feature of multiferroic material is having a coupling of two order parameters. Magnetoelectric coupling especially are of interest for memory and logic device applications as mentioned earlier. BiFeO$_3$ is multiferroic material that shows magnetoelectric coupling between antiferromagnetism and ferroelectricity. Chu et al.[33] has demonstrated the possibility of magnetoelectric random access memories (MER-AMs) by using heterostructure consisting of a ferromagnet (CoFe) in contact with the BiFeO$_3$. Switching of BiFeO$_3$ using electric field determined magnetization direction of CoFe layer. Another good example of using multiferroic for spintronic application is shown by Gajek et al.[34]. They have demonstrated four-state memory device using ultrathin single phase multiferroic film, La$_{0.1}$Bi$_{0.9}$MnO$_3$, as a barrier in spin-filter-type tunnel junctions. Four-state memory is realized by having two direction of electric polarizations in combination with two direction of magnetization. Four state logic or even higher state logic offers exponential increase of computing capacity.

Recently, a new kind of perovskite multiferroic material has been proposed[35]: Insulators that are neither ferroelectric nor ferromagnetic are transformed into ferroelectric ferromagnets using a single control parameter: strain. In 2006, Fennie and Rabe predicted that epitaxial europium titanate (EuTiO$_3$) exhibits strong ferromagnetism with spontaneous magnetization $M_s \sim 7\mu_B$/Eu and strong ferroelectricity with spontaneous polarization $P_s \sim 10\mu C$/cm$^2$ simultaneously under large biaxial compressive strain[35]. These values are orders of magnitude higher than any other known ferroelectric ferromagnets and are comparable or even higher than the materials that are solely ferroelectric or ferromagnetic. Ferroelectric and ferromagnetic ordering not only coexist and are large, but also electrical polarization $P$ and magnetization $M$ are
coupled. In this chapter, firstly, theoretical background of the strained EuTiO$_3$ being multiferroic is introduced. Secondly, structural and ferroelectric characterization from collaborators are briefly discussed. Lastly, this thesis focuses on ferromagnetic characterization using Magneto-Optic Kerr Effect (MOKE).

3.2 Theoretical prediction

In Ref. [35], Fennie and Rabe predicted how magnetization (M) and electric polarization (P) can be strongly coupled within a system. In their prediction, strong M-P coupling is associated with a competition between a ferromagnetic (FM)-ferroelectric (FE) state and an antiferromagnetic (AFM)-paraelectric (PE) state. According to their prediction, one of the way to induce such competition is by the interplay of spins, optical phonons, and strain. In order for this proposed mechanism to be realized, they mentioned four criteria that a bulk system must satisfy: “(1) it must be an AFM-PE insulator in which at least one infrared-active (IR) phonon is coupled to the magnetic order, (2) spins in the AFM ground state should be aligned with the application of a magnetic field of modest strength, (3) this alignment should decrease the frequency of the spin-coupled IR-active phonon, and, (4) the key to this approach, the IR-active phonon must be strongly coupled to strain.” Epitaxial strain has been used to enhance the mobility of transistor [36] and increase superconducting [37], ferromagnetic [38, 39] and ferroelectric [40] transition temperature. In their proposal, they used epitaxial strain to dial into the region of the phase diagram where a spin-phonon-driven destabilization of the lattice actually occurs. This results in the FM-FE phase, which competes with the AFM-PE ground state. This competition allows to control magnetic and electric phase by an applied electric and/or magnetic field. The FM-FE
phase can be achieved by the spin-phonon(lattice) coupling as follows.

\[ \omega^2 = \omega_0^2 - \lambda \langle S_i \cdot S_j \rangle \]  

Here \( \omega \) is the frequency of an IR-active phonon mode, \( \omega_0 \) is the bare phonon frequency, \( \lambda \) is the macroscopic spin-phonon coupling constant and \( \langle S_i \cdot S_j \rangle \) is the nearest-neighbor spin-spin correlation function. This spin-phonon coupling, combined with strain, could tune multiple ferroic order parameters simultaneously, and leads to FM-FE phase as a new ground state.[35]. The tuning behavior can be described by the Landau free energy as follows[41].

\[ F(M, P) = \frac{A_P P^2}{2} + \frac{A_M M^2}{2} + \frac{B_P P^4}{4} + \frac{B_M M^4}{4} - |\lambda'| M^2 P^2 \]  

\[ F(L, P) = \frac{A_P P^2}{2} + \frac{A_L L^2}{2} + \frac{B_P P^4}{4} + \frac{B_L L^4}{4} + |\lambda'| L^2 P^2 \]  

Here \( F \) is the Landau free energy, \( P, M \) and \( L \) are the ferroelectric, ferromagnetic and antiferromagnetic order parameters, respectively, and \( A_P, B_P, A_M, B_M, A_L \) and \( B_L \) are expansion coefficients. The sign and strength of the biquadratic coupling coefficient, \( \lambda' \), which is positive for antiferromagnetic order and negative for ferromagnetic order, originates in the spin-phonon coupling and is fundamental to the tuning behavior. Such biquadratic magnetoelectric coupling, as well its change of sign under magnetic bias, was recently confirmed for unstrained bulk EuTiO\(_3\) and was found to be large[42].

It was theoretically predicted that FM-FE ground state can be achieved with either biaxial tension of \( \epsilon_s = +0.75\% \) or biaxial compression \( \epsilon_s = -1.2\% \) (see Fig.3.1(a)). Biaxial tension rather than biaxial compression is chosen here since FM-FE ground state can be achieved with lower biaxial strain. Due to the fact that it is very difficult to find appropriate substrate to meet such qualifications and maintaining a high-crystalline quality of the film with reasonable thickness in such high stress is
Figure 3.1: Epitaxial phase diagram of EuTiO$_3$ and schematic diagram of crystal structure of strained EuTiO$_3$ on DyScO$_3$. (a) Epitaxial phase diagram of EuTiO$_3$ strained from $-2\%$ (biaxial compression) to $+2\%$ (biaxial tension). EuTiO$_3$ with biaxial strain between $\epsilon_s = -1.2\%$ and $\epsilon_s = 0.75\%$ has AFM+PE ground state. EuTiO$_3$ with biaxial tensile strain more than $\epsilon_s = +0.75\%$ or with biaxial compressive strain more than $\epsilon_s = -1.2\%$ has FM+FE ground state. (b) Schematic diagram of unstrained bulk EuTiO$_2$ and (c) epitaxially strained thin-film EuTiO$_3$ on the DyScO$_3$ substrate, showing the in-plane expansion due to biaxial tensile strain. The diagram was taken from Ref.[41]

not trivial, Lee et al. explored substrates that could give biaxial tension just above $\epsilon_s = +0.75$. They found that that EuTiO$_3$ grown on dysprosium scandate(DyScO$_3$) substrate experiences $\epsilon_s = +1.1\%$ biaxial tensile strain[41]. With such strain, films can be grown thick enough that ferroelectricity and ferromagnetism can be measured without destroying crystalline quality of the EuTiO$_3$ film. This approach is illustrated in Fig.3.1(b) and (c).
3.3 Commensurate epitaxial growth of europium titanate and its ferroelectric characterization from collaborators

3.3.1 Structural properties of epitaxially strained Europium Titanate

Commensurate epitaxial (001) EuTiO$_3$ films with a thickness of 22nm were grown by Lee et al.[43] using reactive molecular beam epitaxy (MBE) on (001) LSAT$^1$, (001) SrTiO$_3$, and (110) DyScO$_3$ substrate. It is important to grow defect-free, epitaxial EuTiO$_3$ film to study intrinsic multiferroic properties since unstrained epitaxial EuTiO$_3$ could exhibit ferromagnetism which arises from extrinsic effect[43]. Extrinsic effects are known to occur in thin films, particularly for deposition technology involving energetic species, which can induce defects. After the sample was grown, high-resolution X-ray diffraction (by Lee et al.) and cross-sectional scanning transmission electron microscopy (STEM) (by Kourkoutis et al.) was performed to characterize structural properties of EuTiO$_3$ films grown on the various substrates. It was reveal the films was commensurate, smooth and of high structural perfection without any defect or dislocation[41].

3.3.2 Ferroelectricity of strained Europium Titanate

Vlahos et al. used second harmonic generation (SHG) technique to measure ferroelectricity of the strained europium titanate (EuTiO$_3$) film. Fig.3.2(a) shows temperature dependent SHG measurements indicating that the paraelectric-to-ferroelectric transition temperature ($T_c$) of the films is 250K. Other control samples do not show any response to SHG measurement. The absence of an SHG response from the EuTiO$_3$

$^1$ (LaAlO$_3$)$_{0.29}$(SrAl$_{0.5}$Ta$_{0.5}$O$_3$)$_{0.71}$
strained at $\epsilon_s = -0.9\%$ (EuTiO$_3$-on-LSAT) and $\epsilon_s = 0.0\%$ (EuTiO$_3$-on-SrTiO$_3$) indicates that EuTiO$_3$ in these strain states is not ferroelectric. Fig.3.2(b) shows the SHG intensity as a function of applied in-plane electric field. It shows dynamics of ferroelectric domains in the EuTiO$_3$-on-DyScO$_3$ sample. Having determined that the EuTiO$_3$ film strained at $\epsilon_s = +1.1\%$ (EuTiO$_3$-on-DyScO$_3$) is potentially ferroelectric, the dielectric constant was measured as a function of temperature in a strained EuTiO$_3$-on-DyScO$_3$ film (Fig.3.2(c)). $T_c$ found by the dielectric constant measurement as a function of temperature is in a good agreement with the $T_c$ found by the SHG technique.

3.4 Ferromagnetism of strained Europium Titanate

3.4.1 Motivation of using Magneto-Optical Kerr Effect

Testing for ferromagnetism in strained EuTiO$_3$-on-DyScO$_3$ films is complicated by the magnetic properties of DyScO$_3$ substrate. Single crystal DyScO$_3$ is known to have a strong magnetocrystalline anisotropy with an easy axis along the [100] direction and a hard axis along the [001] direction[44]. Ke et al.[44] measured the field dependence of magnetization $M$ at $T = 1.8K$ and $T = 10K$ with the magnetic field applied along the [100], [010], [001], [110], and [110] directions (Fig.3.3 (b) and (c)). Based on this measurement one can say that [100] is the easy axis and [001] is the hard axis. They also found a phase transition to long range antiferromagnetic ordering at $T_N \sim 3.1K$ (Fig.3.3(a)). Fig.3.3(b) and (c) show the field dependence of magnetization measurement. At $T = 1.8K$, $M$ increases linearly at low field followed by a steeper increase around 0.3T and finally saturates at high field(Fig.3.3(b)). This is due to spin-flop transition, which is given by antiferromagnetic ordering. However, at $T = 10K$ which is well above the $Néel$ temperature, $M$ is linear to the field for low fields and then approaches saturation values close to those at 1.8K(Fig.3.3(c)). This is
Figure 3.2: Ferroelectricity of EuTiO$_3$-on-DyScO$_3$ below $T_c \approx 250$K. (a) Temperature dependence of the SHG signal of EuTiO$_3$-on-DyScO$_3$ (red), EuTiO$_3$-on-SrTiO$_3$ (blue) and EuTiO$_3$-on-LSAT (green). (b) SHG hysteresis loop (top) and corresponding polarization loop (bottom) for EuTiO$_3$-on-DyScO$_3$ at 5K. This reveals the dynamics of ferroelectric domain in EuTiO$_3$-on-DyScO$_3$. (c) Dielectric constant as a function of temperature for EuTiO$_3$-on-DyScO$_3$, determined by far-infrared reflectance spectroscopy. $T_c$ appears at 250K, which is in good agreement with the value found by the SHG technique in (a). The figures were taken from Ref.[41]
Figure 3.3: Antiferromagnetic nature of DySc\(_3\)O\(_3\). (a) The temperature dependence of the dc susceptibility of DySc\(_3\)O\(_3\) with a 100Oe field applied along [110] crystalline direction. (b) and (c) The field dependence of the magnetization at \(T = 1.8\)K (b)and 10K (c) with the magnetic field applied along the indicated crystalline directions. The figures were taken from Ref.[44].

Typical paramagnetic behavior. In either case, magnetic moment is very high (\(\approx 9\mu_B/\text{Dy}\)) at high magnetic field. If bulk material is used for a measurement, magnetic moment could still be quite significant even at low field.

These magnetic properties of DySc\(_3\)O\(_3\) as a substrate material give us two concerns. First, magnetization anisotropy is strong enough that it could physically crack or rotate when magnetic fields above a few tesla are applied. We have experienced that the sample actually shattered when we applied more than a couple of tesla and thus, it requires extra care for high field measurement. Secondly, when thin ferromagnetic film
is grown on top of this thick substrate, paramagnetic or antiferromagnetic response
swamps the signal from the thin ferromagnetic film if SQUID magnetometer is used.
Thus, it is crucial to use surface sensitive technique such as Magneto-Optical Kerr
Effect (MOKE) to probe the thin ferromagnetic film only. MOKE technique is good
only for qualitative measurement and requires to use other techniques like SQUID
magnetometry for quantitative analysis. Once the ferromagnetic signal is measured
by MOKE, this data can guide SQUID magnetometry measurement to find the signal
from EuTiO$_3$ film. SQUID magnetometry data was taken by Ke et al. and this will
be compared with data taken by MOKE as well.

3.4.2 Magneto-Optic Effect

When light interacts with magnetic materials, either polarization or intensity of light
could be linearly proportional to the magnetization of the magnetic materials. It is
called magneto-optic effect. The Kerr effect is a measurement of the reflected light,
while the Faraday effect is a measurement of the transmitted light as illustrated in
Fig.3.4. The Kerr effect is often times called Magneto-Optical Kerr Effect (MOKE).
There are three types of geometry for MOKE measurement: polar, longitudinal, and
transverse. MOKE geometry is defined by the relative orientation of the plane of
the incidence of the light and the magnetization of the material. Polar MOKE is
when the magnetization vector is perpendicular to the reflected surface and parallel
to the plane of incidence. Longitudinal MOKE is when the magnetization vector is
parallel to both the reflected surface and the plane of incidence. Both polar MOKE
and longitudinal MOKE is a rotation of the polarization of the light proportional
to the component of the magnetization. Transverse MOKE is when the magnetiza-
tion is parallel to the reflected surface and perpendicular to the plane of incidence.
Transverse MOKE is a change in reflectivity of the reflected light proportional to the
Faraday effect

Kerr effect

Figure 3.4: Illustration of Magneto-Optic effect. Kerr effect is a measurement of the reflected light and Faraday effect is a measurement of the transmitted light.

component of the magnetization. Since EuTiO$_3$-on-DyScO$_3$ has the easy axis parallel to the sample surface, longitudinal MOKE is used here. Magneto-Optic effect comes from birefringence of material which is dependent on a magnetic field inside material. Classically speaking, individual electrons in the medium have a slightly different response to right- and left-handed circularly polarized light in the presence of a longitudinal field. The electromagnetic force acting on an electron in the presence of magnetic field is given by equation of motion.

\[
m\ddot{r} + m\omega_0^2 r = -e(Ee^{i(kz-\omega t)} + \frac{v}{c} \times B\hat{z})
\]  

(3.3)
Using the trial solution \( r = r_0 e^{i(kz - \omega t)} \), we find

\[
  r_{0\pm} = -\frac{e}{m} \frac{E_\pm}{m\omega_0^2 - \omega^2 \mp \omega \omega_H}
\]  

(3.4)

where \( r_{0\pm} = (x \pm iy)/\sqrt{2} \) and \( E_{\pm} = (E_x \pm iE_y)/\sqrt{2} \). \( E_+ \) corresponds to right-handed circularly polarized light and \( E_- \) corresponds to left-handed circularly polarized light. \( r_+ \) and \( r_- \) corresponds to circular electron motion likewise. \( \omega_H = eB_0/mc \) is the cyclotron frequency of an electron in the static magnetic field \( B_0 \). This can be deduced to the dielectric constant of the medium for right- and left-handed circularly polarized light.

\[
  \epsilon_{\pm} = n_{\pm}^2 = \frac{k_{\pm}^2 c^2}{\omega^2} = 1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2 \mp \omega \omega_H}
\]  

(3.5)

This indicates that, in a magnetized medium, right and left-handed circularly polarized light propagate with slightly different indices of refraction or wavenumbers. Quantum mechanically speaking, electrons are excited to conduction band according to selection rules. When material is magnetized, spin subbands have different population in the conduction band. If the spin subband corresponding to left-handed circularly polarized light has more population, its absorption spectrum would be shifted to higher energy due to its state availability. This leads to shift of index of refraction as well. Detailed discussion of classical picture and quantum mechanical picture can be found elsewhere[45, 46]. Since linearly polarized light is superposition of right- and left-handed circularly polarized light, it results in the rotation of linear polarization axis. The angle of rotation is proportional to difference of indices of refraction or difference of wavenumbers which are proportional to magnetization of the material. It is also proportional to propagation depth of light which is thickness of the material for Faraday rotation and penetration depth for Kerr rotation.
3.4.3 MOKE setup

The measurements were carried out in collaboration with Prof. Johnston-Halperin’s group. The details of the experimental setup is as follows. Ti:sapphire laser (Mira, Coherent) produces cw-laser light with the wavelength $\lambda$ tunable from 700nm to 950nm. For this measurement, the wavelength of the laser was tuned to 700nm due to the fact that the transitivity of the DyScO$_3$ is maximum around $\lambda = 700$nm as shown in Fig.3.5[47]. Since direct bandgap of the EuTiO$_3$ is 0.93eV[43], $\lambda = 700$nm was chosen to maximize the absorption in the EuTiO$_3$ while minimizing interactions with the DyScO$_3$ substrate. This renders the measurement insensitive to the paramagnetic substrates as well as to the antiferromagnetic state of DyScO$_3$ below its Néel temperature, $T_N \sim 3.1$K.

The measurement geometry is shown in Fig.3.6. $\lambda = 700$nm probe beam is mod-
ulated by optical chopper (MC1000A, Thorlabs) at 1kHz which is placed at the focus of a pair of lens and then prepared in s-polarization using Glen-Laser polarizer. Then the probe beam is focused onto surface of the samples at about 15° from the plane of the samples. For this measurement, the samples are mounted so that the field is applied in the plane of the sample with the face of the sample positioned at the eucentric point of the cryostat (Spectromag, Oxford). The cryostat is capable of producing magnetic fields up to ±8T using a split coil superconducting magnet. Variable temperature insert (VTI) can set temperature down to 1.2K. Due to the fact that the DyScO$_3$ has large magnetic anisotropy as discussed in Sec.3.4.1 and possibly large magnetostriction, bare DyScO$_3$ and EuTiO$_3$-on-DyScO$_3$ samples tend to fracture in high magnetic fields if they are mounted directly to the copper sample stage. As a result, the samples are mounted using spring clamps that allow for modest distortion of the sample while holding them securely in place for optical measurements as shown in Fig.3.6. This allows the probe light to pass directly through the cryostat by reflecting at a glancing angle from the sample surface. This geometry maximizes the sensitivity of the probe light to the in-plane component of the sample magnetization during the application of the in-plane magnetic field.

After the beam is reflected from the surface of the sample, it is collimated and goes through variable waveplate (custom-built, Meadowlark), which is set to be half-wave plate for 700nm, to rotate the polarization to be at 45°. This is tuned with non-magnetic sample. Then, the beam is split into s and p polarization using Glen-Laser polarizer and focused onto A and B channel of the home-built balanced amplified photodetector, respectively. Circuit diagram of the balanced amplified photodetector is shown in Fig.3.7. Noise characteristics of the photodetector is similar to the one which can be found in Ref.[46]. A-B signal from the balanced amplified photodetector goes into the voltage preamplifier (SR560, Stanford Research) and then finally into
Figure 3.6: MOKE setup for EuTiO$_3$-on-DyScO$_3$ experiment.

a lock-in amplifier (7265, Signal Recovery) while the sum signal is also measured to calculate the rotation angles. This measures the Kerr angle, $\theta_{\text{Kerr}}$, the difference in polarization angle between the incident and reflected probe. This rotation is proportional to the product of the magnetization and the dielectric tensor of the sample, making a quantitative determination of the magnetization difficult, but allowing for the quantitative evaluation of the coercivity and systematic behavior such as the temperature dependence.

### 3.4.4 Data processing

The data is processed as follows: Fig.3.8(a) is raw data from a single field sweep at a temperature of 2K. The field is swept from -50Oe to +50Oe and back to -50Oe. When the field comes back to -50Oe, the signal does not exactly reproduce due to a linear drift in time. This linear drift is subtracted to generate the data shown in Fig.3.8(b). Finally, the offset is set to zero and five full field scans are averaged to
and a hole for the two photodiodes

NOTE: mount board radiation with BNCs and Banana conn on box

Wires to three panel-mount BNCs

Photodiode Bridge Circuit V.2

POWER IN +/- 15v

Min +/- 4.5v

Max +/- 18v

Datasheet for Op Amp OPA627:

Figure 3.7: Photodiode bridge circuit diagram[46]
Figure 3.8: Analysis of the MOKE data taken from EuTiO$_3$-on-DyScO$_3$. (a) Raw data from a single MOKE scan (-50Oe to +50Oe to -50Oe). (b) A linear drift in time is subtracted so that the first and last data points coincide. (c) The offset in $\theta_{\text{Kerr}}$ is subtracted so that the loop is symmetric and five individual scans are averaged. Excellent reproducibility in $H_c$ prevents significant broadening of the magnetization reversal.

improve the signal-to-noise, as shown in Fig.3.8(c). Note that despite the averaging, the magnetic field reversal does not show noticeable broadening, indicating excellent reproducibility in coercive field $H_c$. 
3.4.5 Ferromagnetism of strained Europium Titanate

Magnetic field dependence of ferromagnetism

The MOKE response at a temperature of 2K from all three EuTiO$_3$ films and a bare DyScO$_3$ substrate is shown in Fig.3.9. All the $\theta_{Kerr}$ curves are obtained after data processing described in the previous section. The EuTiO$_3$ strained by $\varepsilon_s = +1.1\%$ (EuTiO$_3$-on-DyScO$_3$) exhibits a clear ferromagnetic hysteresis loop, with sharp switching to full saturation, signifying that it is ferromagnetic in contrast to the EuTiO$_3$ with $\varepsilon_s = -0.9\%$ (EuTiO$_3$-on-LSAT) or $\varepsilon_s = 0.0\%$ (EuTiO$_3$-on-SrTiO$_3$).
shown by the dashed line in Supplementary Fig. 9. The model fits well with the experimental curve and yields a $T_c$ of 4.24±0.02 K and a critical exponent $\nu$ of 0.42±0.02, in reasonable agreement with the theoretical estimate of 0.5 for a three dimensional ferromagnet.

The coercivity, $H_c$, is also extracted from the magnetization curves for all temperatures. As shown in Supplementary Fig. 9, $H_c$ monotonically decreases with increasing temperature, consistent with the $T_c$ calculated above. While far from exhaustive, this analysis supports the assertion that EuTiO$_3$ is a well behaved ferromagnet for a biaxial strain of +1.1%.

Figure 3.10: Temperature dependence of the remanent Kerr angle and coercivity for EuTiO$_3$-on-DyScO$_3$. (a) Magnetic field dependent MOKE measurement taken from EuTiO$_3$-on-DyScO$_3$ in various temperature. At all temperature except 5K clear hysteresis loop is observed. (b) Temperature dependence of the remanent Kerr angle and coercivity for EuTiO$_3$-on-DyScO$_3$. Error bars represent one sigma variation for temperature, $\theta_{Kerr}$, and $H_c$. The dashed line is a power law fit to $\theta_{remanent}$ and yields a $T_c$ of 4.24±0.02K and a critical exponent of 0.42±0.02, consistent with the theoretical prediction of 0.5 for a three dimensional ferromagnet.

**Temperature dependence of ferromagnetism**

Due to linear drifts in time (see Fig.3.8(a)), simply monitoring $\theta_{Kerr}$ as a function of temperature is not practical. As a result, the temperature dependence is determined by taking a series of hysteresis curves from low to high temperature. MOKE signal at different temperatures from 1.64K to 5K are shown in Fig.3.10(a). The magnetization shows sharp switching and full saturation up to $T_c = 4.24$K. As temperature increase, hysteresis loop is reduced: both remanent Kerr angle and the coercive field is reduced. Remanent Kerr angle and coercive field was extracted from the magnetization curves for all temperatures. The remanent Kerr angle $\theta_{remanent}$ is calculated from $\theta_{remanent} = (\theta_{remanent}(+H) - \theta_{remanent}(-H))/2$ and the coercive field $H_c$ was calculated from $H_c = H(\theta_{Kerr}=+0) - H(\theta_{Kerr}=-0)$. As shown in Fig.3.10(b), the remanent Kerr
angle monotonically decreases as temperature is increased until, above a temperature of about 4.3K, the signal-to-noise ratio of the remanence drops below one. The data is fit to a power law of the form:

\[ M(T) = M_0(T_c - T)^\beta \]  

shown by the dashed line in Fig.3.10(b). The model fits well with the experimental curve and yields a \( T_c \) of 4.24 ± 0.02K, which is slightly lower than 5.5K, the Néel temperature of unstrained EuTiO₃[43], and a critical exponent \( \beta \) of 0.42 ± 0.02, in reasonable agreement with the theoretical estimate of 0.5 for a three dimensional ferromagnet[48]. Fig.3.10(b) also shows that \( H_c \) monotonically decreases with increasing temperature, consistent with the \( T_c \) calculated above. While far from exhaustive, this analysis supports the assertion that EuTiO₃ is a well behaved ferromagnet for a biaxial strain of \( \epsilon_s = +1.1\% \).

**Comparing with SQUID magnetometry**

Because the MOKE measurements of ferromagnetism are not on an absolute scale, we used SQUID measurements to quantify the spontaneous magnetization of EuTiO₃ strained at \( \epsilon_s = +1.1\% \) (Fig.3.11). Ke et al. performed SQUID measurement in nominally zero residual magnetic field to minimize the paramagnetic response of the substrate. The strained EuTiO₃ is cooled in a 100Oe field, which is high enough to polarize the EuTiO₃ film yet small enough to minimize the residual magnetic field during subsequent SQUID measurements. In agreement with the MOKE results, clear hysteresis loops are observed below 4K after subtracting paramagnetic or antiferromagnetic background signal, and the spontaneous magnetization of the strained EuTiO₃ is seen to be large, that is, about 3\( \mu_B \)/Eu as shown in Fig.3.9(a). This is only about a factor of two to three difference from the predicted value (7\( \mu_B \)/Eu. As shown
in Fig.3.11(b) and Fig.3.12, the observed magnetization rise at the same temperature ($T_c$) as the MOKE signal and follows it until the antiferromagnetic transition of the DyScO$_3$ substrate occurs, at 3.1K, where the substrate signal masks the magnetization of the strained EuTiO$_3$ film. Polarized X-ray measurements of the local moment connect the observed magnetism with that of Eu$^{2+}$ (Supplementary Discussion 4 in Ref.[41]). From the combination of these results, and because the ferromagnetism occurs well above the antiferromagnetic transition of the DyScO$_3$ substrate, we conclude that the observed ferromagnetism is not correlated with the magnetic ordering of the underlying substrate.

### 3.4.6 Magnetolectric coupling

Bulk EuTiO$_3$ exhibits a decrease in its dielectric constant as it is cooled through its antiferromagnetic transition[49]. Owing to the change in the sign of the spin-
spin correlation function in Eq.3.2 when strained EuTiO\textsubscript{3} becomes ferromagnetic, the dielectric constant of EuTiO\textsubscript{3}-on-DyScO\textsubscript{3} should increase as the film is cooled through its ferromagnetic transition. Ke et al. showed such behavior by measuring capacitance as a function of temperature (Fig.3.13). \(T_c\) appears near 4.2K, which is in good agreement with MOKE and SQUID data (Fig.3.12). This further confirms the ferromagnetic transition in commensurately strained EuTiO\textsubscript{3}-on-DyScO\textsubscript{3} and its strong spin-lattice coupling.

### 3.5 Conclusion

We successfully demonstrated ferromagnetic properties of EuTiO\textsubscript{3}-on-DyScO\textsubscript{3}, which is in high biaxial tensile strain \((\epsilon_s = +1.1\%)\) using MOKE measurement. In conjunction with the works of collaborators, this is indeed a multiferroic material with
Figure 3.13: Temperature dependence of the capacitance of EuTiO$_3$-on-DyScO$_3$ near $T_c$. The capacitance of a bare DyScO$_3$ substrate measured under the same conditions is also shown. The figure was taken from Ref.[41].

FE-FM ground state below 4.2K. This results confirm the predicted mechanism[35] and open the door to higher temperature implementations of strong ferromagnetic ferroelectrics[50], which would allow for dramatic improvements in numerous devices and applications.
Chapter 4

Optical spin polarization and readout of nitrogen-vacancy (NV) centers in diamond

There’s Plenty of Room at the Bottom

Richard P. Feynman

4.1 Introduction

There has recently been a lot of attention to carbon-based materials such as bucky-balls, nanodiamonds (0 dimensional), carbon nanotubes (1 dimensional), graphene (2 dimensional) and bulk diamond (3 dimensional), in various areas of science. Although diamond has been investigated less rigorously than carbon nanotubes and graphene, it has been used in many different fields for various reasons. For example, its mechanical hardness makes useful diamond-coated or diamond fabricated cantilevers[51]. Its radiation hardiness, large bandgap, small dielectric constant, and excellent heat conductance make diamond a good candidate for a radiation detector[52]. Since a method of diamond synthesis was developed in 1950s and quality control and mass production has been achieved, a lot of opportunities have opened up to scientists. It
is now well known that single crystalline diamond can be synthesized both at high pressure and high temperature (HPHT) in the diamond stable region of the carbon phase diagram and at low pressure in the graphite stable region of the phase diagram using chemical and physical vapor deposition techniques. Most of thin film diamond is grown by chemical vapor deposition (CVD) while bulk diamond is synthesized by either CVD or HPHT. Although pure diamond has a band gap of 5.5eV which makes it a good insulator, impurities in diamond form discrete energy states in the gap and electrons can be excited to higher states by visible light. Once electrons are excited, they relax to lower states by emitting photons of which wavelength is set by the difference of the ground state and the excited state. Thus, color of diamond is given by its impurities. For instance, blue diamond has boron impurities and yellow diamond corresponds to nitrogen impurities. Pink, which is one of the most popular colors for diamond as a gemstone, is given by nitrogen-vacancy (NV) impurity center in diamond, which is a focus of this thesis. Due to their unique electronic structure and spin properties, NV centers in diamond are one of the most attractive candidates for spintronic applications, such as quantum computation and high sensitivity magnetometry. Given the fact that this is a new field of research, there is much to be explored, in terms of both material studies as well as applications. In the following sections, the physical, electronic and optical properties of NV centers in diamond are reviewed in the context of its applications in spintronics. Then I demonstrate vector magnetometry using NV centers in diamond in Chapter 5 and proposed biological applications of the magnetometry using NV centers in Chapter 6.

4.2 Why nitrogen-vacancy centers in diamond?

Why are NV centers in diamond such an attractive system? First, an NV center is a very stable single photon source. No bleaching or quenching of the fluorescence has
been reported, although blinking only has been reported from 5nm size detonation nanodiamond[53]. Even then, it is possible to control this blinking by modifying the surface of the nanodiamond. By combining with the fact that nanodiamonds are biologically friendly, the photo-stability gives this system a huge advantage over quantum dots. Nanodiamonds with NV centers have been used in bio-labelling[54], cell-tracking[55], etc. Second, NV centers have excellent spin properties. The spins in this system can be polarized by optical pumping, which can be done with a far-field optical setup. This system has highly localized electronic bound states, which means that spins are isolated from sources of decoherence. The defect states do not interfere with electronic states of the host material, diamond, which has bandgap of 5.5eV. However, the energy difference between the ground and excited state is large enough to avoid thermal excitation between them. Small spin-orbit coupling of diamond and a weak nuclear spin bath increases the spin lifetime. Thus, the spin state of an NV center is robust enough that experiments on this system can be conducted in room temperature with excellent field sensitivity down to a few nano-Tesla, which is useful for magnetometry applications[56]. Additionally, due to the fact that NV centers have four possible orientations due to the tetrahedral structure of the carbon lattice, vector-field magnetometry is also possible. These spin properties make NV centers an excellent candidate for quantum computing as well[57].

4.3 Atomic structure of NV center

A NV center is a deep point defect in a diamond crystal lattice. It consists of a nitrogen atom, which substitutes a carbon atom, and a lattice vacancy right next to the nitrogen atom forming nearest-neighbor pair as shown in Fig.4.1. Because diamond has tetrahedral structure, there are four possible orientations of the NV centers: [111], [111], [111], and [111] (Fig.4.1(a)). A nitrogen atom reduces the tetrahedral
Figure 4.1: Atomic structure of NV centers. (a) Crystal structure of diamond having NV centers with four different orientations. Gray and yellow spheres represent carbon atoms and nitrogen atoms, respectively. Pink bars indicate NV crystal axes along [111], [111], [111], and [111]. (b) Molecular structure of negatively charged NV center with a crystal axis along [111]. Pink and gray envelops represent $sp^3$ orbitals associated with a nitrogen atom ($n$) and carbon atoms ($c_1$, $c_2$, and $c_3$). Number of electrons available to occupy the orbitals are six: a nitrogen atom contributes two electrons, three of each carbon atoms contribute one each and one electron comes from the environment (given by the abundant nitrogen atoms as a donor in the crystal).

Symmetry of diamond to a trigonal $C_{3v}$ symmetry, with the nitrogen atom and the vacancy forming the NV center crystal axes. Fig.4.1(b) shows molecular structure of a negatively charged NV center. There are six electrons available to occupy the orbitals. The nitrogen atom contributes two electrons, the three carbon atoms each contribute one electron and one electron comes from the surrounding environment because the abundant nitrogen atoms act as donors in the crystal. This even number of electrons forms a system with a total spin of 1.
4.4 Vibronic structure of NV center

Fig.4.2(a) shows energy diagram of an electronic transition of an NV center with phonon coupling along the generalized coordinate \( q \), a normal mode of the lattice. Absorption and emission of a photon involves a electrons transition between the ground state and the excited state. The electron transition probability is proportional to the overlap of the electron wavefunctions in the ground state and the excited state. When a photon is absorbed to or emitted from the NV center, the most intense transition does not involve phonons, according to the Franck-Condon principle. This is shown by green (for absorption) and red (for emission) arrows. When a photon is absorbed causing electron transition from the ground state to the excited state, the electron quickly decays to its zero point lattice vibration level of the excited state by means of a non-radiative process. When the electron directly relaxes to the zero point lattice vibration level of the ground state by emitting a photon, it is called a zero phonon line (ZPL). The difference of a normal mode of the lattice between the ground state and the excited state proportionally increases as a function of temperature. Thus, transition probability is usually small at room temperature due to the less overlap of the electron wavefunction, but becomes bigger as the system is cooled. The shape of the ZPL is Lorentzian with a width determined by the excited state lifetime according to the Heisenberg uncertainty principle. When an electron transitions from the zero point lattice vibration level of the excited state to the zero point lattice vibration level of the ground state is by emitting phonons, the corresponding photon emission forms phonon sidebands in the emission spectrum. The difference between a maximum of phonon sideband (transition without phonon) and a ZPL, a Frank-Condon shift, is found to be 0.14eV at room temperature. The typical emission spectrum of NV centers given by the vibronic structure is shown in Fig.4.2(b).
Figure 4.2: Vibronic structure of NV center. (a) Energy diagram of an electronic transition with phonon coupling along the generalized coordinate $q$, a normal mode of the lattice. The green upward arrow represents absorption without phonons. The red downward arrow represents the symmetric process in emission. The orange downward dotted arrow shows emission corresponding to zero phonon line (ZPL). (b) Typical optical spectrum of NV centers in diamond. A peak at 637nm corresponds to the ZPL.

4.5 Electronic structure of NV center

4.5.1 Orbital structure of NV center

When only a vacancy center exists, it forms tetrahedral symmetry. As a nitrogen atom is introduced right next to the vacancy, the tetrahedral symmetry is reduced to $C_{3v}$ symmetry. In order to understand ordering of the energy states, we need to understand configurations of molecular orbitals (MO) of the system with symmetry considerations. The MO and state configurations of NV centers were initially developed by Lenef and Rand[58] using linear combinations of atomic orbitals (LCAO). MOs with $C_{3v}$ symmetry were constructed by linearly combining one $sp^3$ nitrogen orbital ($n$) and three $sp^3$ carbon orbitals ($c_1$, $c_2$, and $c_3$) neighboring the vacancy as shown in Fig.4.1(b). Two $A_1$ symmetric MOs (labeled as $a_1(N)$ and $a_1(C)$) and two
$E$ symmetric MOs (labeled as $e_x$ and $e_y$) were identified and ordered energetically by considering symmetry and charge overlap. These MOs are written as follows.

\[ a_1(N) = n \]  
\[ a_1(C) = \frac{1}{\sqrt{3(1 + 2S_{cc} - 3S_{nc}^2)}}(c_1 + c_2 + c_3 - 3S_{nc}n) \]  
\[ e_x = \frac{1}{\sqrt{3(2 - 2S_{cc})}}(2c_1 - c_2 - c_3) \]  
\[ e_y = \frac{1}{\sqrt{2 - 2S_{cc}}}(c_2 - c_3) \]

where $S_{nc} = \langle n|c_1 \rangle$ and $S_{cc} = \langle c_1|c_2 \rangle$ are orbital overlap integrals. The LCAO method is a highly approximate method of constructing the MOs because it uses a restricted basis set and does not consider the interactions between the MOs of the defect center and the electron orbitals of the remainder of the crystal. However, it is still a good method to estimate the symmetry type and energy ordering. Later these MOs were modified by Hossain et al.\cite{59} using ab initio density functional theory (DFT). The studies found that the $a_1(N)$ and $a_1(C)$ MOs are mixed to form $a_1$ and $a'_1$ and $a'_1$ has been forced downwards in energy into the valence band of the diamond and $a_1$ has significant contributions from both the nitrogen and carbon atomic orbitals. Thus there exist three MOs only within the diamond bandgap: \{a_1, e_x, e_y\}. This is shown in Fig.4.3(a). Fig.4.3(b) shows the electron density isosurfaces for each of the calculated single electron states by the ab initio method\cite{59, 60}. This clearly shows that $a_1$ has contributions from both nitrogen atom and three carbon atoms and $e_x$ and $e_y$ has contributions only from carbon atoms.

By applying the Pauli exclusion principle and Hund’s rule, we can now identify spin configurations of the ground state and the excited state. The ground MO configuration is $a'_1a_1^2e^2$ and the first excited MO configuration should be $a'_1a_1^2e^3$. There are several second excited MO configurations: $a'_1e^4$, $a'_1a_1^2e^3$ and $a'_1a_1^2e^4$. These second
linear combinations of products of two MOs are representations and Clebsch–Gordan coefficients defined in [13]. Schematics of the three MOs in the region of the vacancy and their energy ordering are expected to contribute to the observable properties of the centre. Consequently, only the second excited MO configurations are described by Eqs.4.1. The states of these second excited MO configurations could be close in energy and the majority of these second excited MO configurations are in the bandgap of diamond and that these resemble the highly localized MOs that have significant contributions from both the nitrogen and carbon atomic orbitals.

Using the ab initio six-electron model of the NV centre and the electron orbitals of the remainder of the crystal, the LCAO method is a highly approximate method of constructing the MOs as it does not consider the interactions between the MOs of the defect and the atom colours are the same as in Fig. 4.1 and a vacancy is depicted by a white sphere. Consequently, only the second excited MO configurations are described by Eqs.4.1. The states of these second excited MO configurations could be close in energy and the majority of these second excited MO configurations are in the bandgap of diamond and that these resemble the highly localized MOs that have significant contributions from both the nitrogen and carbon atomic orbitals.

Conduction band

Valence band

\[ e_x \quad \quad a_1 \quad \quad e_y \]

\[ a_1' \]

Figure 4.3: Molecular orbital structure of NV center. (a) Molecular Orbital (MO) state ordering of NV center. \( a_1' \) is below the valence band maximum, \( a_1 \) (highest occupied MO) and \( e_x \) and \( e_y \) (lowest unoccupied MOs and are degenerate) are in the bandgap of diamond. (b) Electron density isosurfaces of \( a_1 \) (left), \( e_x \) (middle) and \( e_y \) (right). The figure was adopted from Ref.[60]. Red and blue components represent positive and negative contributions to the MOs, respectively. MO isosurfaces of \( e_x \) and \( e_y \) are described by Eqs.4.1. The atom colors are the same as in Fig.4.1 and a vacancy is depicted by a white sphere.
excited MO configurations do not play a significant role and contribute only minimally to the observable properties of the NV center. However, it could be mixed with the ground and the first excited MOs and shift their energies. Therefore, we will only consider the ground and the first excited MO configurations here. The resulting state configurations \(|s_{Li}^{s}; S, m_s\rangle\) are shown in Eq.4.2 and Eq.4.3 using the notation of \(|a_1^1\bar{a}_1^1, a_1\bar{a}_1, e_x\bar{e}_x, e_y\bar{e}_y\rangle\). \(L\) is the Mulliken symbol showing the degeneracy of orbitals (e.g. \(A\): orbital singlet, \(E\): orbital doublet), \(s\) is the spin degeneracy and \(i\) is the symmetry around the \(C_2^*\) axis. MOs without and with an overbar denote spin up and spin down, respectively. For the ground MO configurations \((a_1^2\bar{a}_1^2e^2)\),

\[
|^{3}A_{2}; 1, 0\rangle = \frac{1}{\sqrt{2}}(|11, 11, 10, 01) + |11, 11, 01, 10\rangle) \quad (4.2a)
\]

\[
|^{3}A_{2}; 1, +1\rangle = |11, 11, 10, 10\rangle \quad (4.2b)
\]

\[
|^{3}A_{2}; 1, -1\rangle = |11, 11, 01, 01\rangle \quad (4.2c)
\]

\[
|^{1}E; 0, 0\rangle = \left\{ \begin{array}{c}
\frac{1}{\sqrt{2}}(|11, 11, 11, 00) - |11, 11, 00, 11\rangle) \\
\frac{1}{\sqrt{2}}(|11, 11, 01, 10) - |11, 11, 10, 01\rangle)
\end{array} \right\} \quad (4.2d)
\]

\[
|^{1}A_{1}; 0, 0\rangle = \frac{1}{\sqrt{2}}(|11, 11, 11, 00) + |11, 11, 00, 11\rangle) \quad (4.2e)
\]
For first excited MO configurations \( (a_1^2a_1^e^3) \),

\[
|^{3}E; 1, 0 \rangle = \left\{ \frac{1}{\sqrt{2}} (|11, 10, 01, 11\rangle + |11, 01, 10, 11\rangle) \right\} \quad (4.3a)
\]

\[
|^{3}E; 1, +1 \rangle = \left\{ |11, 10, 10, 11\rangle \right\} \quad (4.3b)
\]

\[
|^{3}E; 1, -1 \rangle = \left\{ |11, 01, 01, 11\rangle \right\} \quad (4.3c)
\]

\[
|^{1}E'; 0, 0 \rangle = \left\{ \frac{1}{\sqrt{2}} (|11, 10, 01, 11\rangle - |11, 01, 10, 11\rangle) \right\} \quad (4.3d)
\]

Hund’s rule indicates that \(^3A_2\) should be the ground electronic state. Since the optical transition is associated with spin triplet state, \(^3E\) is the excited state. There are two spin singlet states, \(^1A_1\) and \(^1E\). \(^1A_1\) state is known to lie between \(^3A_2\) and \(^3E\). However, \(^1E\) state is not observed experimentally and not even clear where it should be positioned. Based on a symmetry argument (discussed in Sec.4.5.2), we will consider \(^1A_1\) state only as a metastable state that lies between \(^3A_2\) ground state and \(^3E\) excited state in this thesis. Additionally, in the first excited MO configuration, Hund’s rules also indicate that \(^1E'\) has a bigger repulsion energy than \(^3E\). Since \(^1E'\) state does not play a role in the NV center property, it will not be considered here. This is summarized in Fig.4.4. The experimentally found energy difference between \(^3E\) and \(^3A_2\) (the optical ZPL) is 1.945eV as shown in Fig.4.2(b).

### 4.5.2 Fine structure of NV center

Spin-spin interaction and spin-orbit interaction have been theoretically studied \([58, 60, 61]\) to understand the spin sublevels of the NV impurity center in diamond and the energy level ordering. Here we will consider spin-spin interaction and spin-orbit
interaction to understand spin sublevels in $^3A_2$ ground state and $^3E$ excited state in a simple manner.

The spin dynamics of an NV center is described by the Hamiltonian.

$$\mathcal{H} = \mathcal{H}_{MO} + \mathcal{H}_{SS} + \mathcal{H}_{SO} + \mathcal{H}_{Zeeman} + \mathcal{H}_{HF}$$  \hspace{1cm} (4.4)$$

$\mathcal{H}_{MO}$ is the term that is determined by molecular orbital bonding considerations and this was covered in Sec.4.5.1. $\mathcal{H}_{SS}$ describes spin-spin interaction and $\mathcal{H}_{SO}$ is determined by spin-orbit interaction. The Hamiltonian also includes a Zeeman energy term, $\mathcal{H}_{Zeeman}$, and hyperfine interaction term, $\mathcal{H}_{HF}$. In this section, hyperfine interaction is ignored for simplicity but is covered later in this section. We have seen in the previous section that an NV center is an $S = 1$ system, $^3A_2$ and $^3E$ are the spin triplet states, and $^1A_1$ and $^1E$ are the spin singlet states. For systems with two or more unpaired electrons, the degeneracy of the spins may be removed even in the absence of external magnetic field. For even total spin number (e.g. $S=1, 2, ...$), this degeneracy is completely lifted in a zero magnetic field. This is called zero field splitting. This is caused by the spin-spin interaction and/or spin-orbit interaction.
3\textsuperscript{A}_2 spin sublevels: Spin-spin interaction

At small distances, two unpaired electrons will experience a strong spin-spin interaction, as shown in Fig. 4.5, due to their magnetic dipole moments. The spin-spin interaction is usually not present in systems with spherical symmetry but does not average out in a non-spherically symmetric systems like those that have C\textsubscript{3v} group symmetry. The 3\textsuperscript{A}_2 state is affected by the spin-spin interaction because it is a spin triplet. (However, spin-orbit interaction does not affect 3\textsuperscript{A}_2 state due to its orbital singlet\textsuperscript{[62][58].}) The spin-spin interaction splits the 3\textsuperscript{A}_2 ground state into a singlet with symmetry A\textsubscript{1} and doublet with symmetry E as follows\textsuperscript{[63]}.

\begin{equation}
A_1 = |A_2, m_s = 0\rangle 
\end{equation} \hspace{1cm} (4.5a)

\begin{equation}
E = \begin{cases} 
|A_2, m_s = 1\rangle 
|A_2, m_s = -1\rangle 
\end{cases} 
\end{equation} \hspace{1cm} (4.5b)

In order to calculate the zero field splitting, we write spin-spin Hamiltonian as follows.

\begin{equation}
\mathcal{H}_{SS} = g_e^2 \mu_B^2 \left[ \frac{\mathbf{S}_1 \cdot \mathbf{S}_2}{r^3} - \frac{3(\mathbf{S}_1 \cdot \mathbf{r})(\mathbf{S}_2 \cdot \mathbf{r})}{r^5} \right] 
\end{equation} \hspace{1cm} (4.6)

Here \( \mathbf{r} \) is a vector joining \( \mathbf{S}_1 \) and \( \mathbf{S}_2 \) as defined in Fig. 4.5. \( \mathbf{S}_i = S_{ix} \mathbf{x} + S_{iy} \mathbf{y} + S_{iz} \mathbf{z} \) where \( i = 1, 2 \) and \( \mathbf{r} = x \mathbf{x} + y \mathbf{y} + z \mathbf{z} \). After a little bit of algebra\textsuperscript{[62]}, this can be

\textsuperscript{2} Suppose an eigenfunction is complex. In this case, there exists at least one other independent eigenfunction with the same energy (complex conjugate). Thus, any state represented by a complex eigenfunction is at least doubly degenerate. Conversely, singlet state must be real. The orbital angular operator \( L_z = i\hbar (x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}) \) is imaginary and has a real eigenvalue since it is a Hermitian operator. Consider the \( L_z |n\rangle = m_l |n\rangle \) operation. If \( |n\rangle \) is singlet state, which is real, \( m_l \) has to be zero to satisfy equality. Thus, orbital singlet should have zero angular momentum.
Figure 4.5: Schematic diagram of spin-spin interaction. \( \mathbf{r} \) is a vector joining \( \mathbf{S}_1 \) and \( \mathbf{S}_2 \).

rewritten as follows.

\[
\mathcal{H}_{SS} = \frac{1}{2} g_e^2 \mu_B^2 \left[ \left( r^2 - 3x^2 \right) S_x^2 + \left( r^2 - 3y^2 \right) S_y^2 \right. \\
+ \left( r^2 - 3z^2 \right) S_z^2 - 3xy(S_x S_y + S_y S_x) \\
- 3xz(S_x S_z + S_z S_x) - 3yz(S_y S_z + S_z S_y) \right]
\]  \hspace{1cm} (4.7)

Eq. 4.7 can be rewritten conveniently in matrix form such as

\[
\mathcal{H}_{SS} = \frac{1}{2} g_e^2 \mu_B^2 \begin{bmatrix} S_x & S_y & S_z \end{bmatrix} \begin{bmatrix} \frac{r^2 - 3x^2}{r^5} & \frac{-3xy}{r^5} & \frac{-3xz}{r^5} \\
\frac{-3xy}{r^5} & \frac{r^2 - 3y^2}{r^5} & \frac{-3yz}{r^5} \\
\frac{-3xz}{r^5} & \frac{-3yz}{r^5} & \frac{r^2 - 3z^2}{r^5} \end{bmatrix} \begin{bmatrix} S_x \\
S_y \\
S_z \end{bmatrix}
\]  \hspace{1cm} (4.8a)

\[
= \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}
\]  \hspace{1cm} (4.8b)

Here \( \mathbf{D} \) is a second-rank traceless tensor and can be diagonalized with the diagonal elements \( D_{xx}, D_{yy} \) and \( D_{zz} \). Then, Eq. 4.7 can be simplified as

\[
\mathcal{H}_{SS} = D_{xx} S_x^2 + D_{yy} S_y^2 + D_{zz} S_z^2
\]  \hspace{1cm} (4.9)

where \( D_{xx} + D_{yy} + D_{zz} = 0 \). \( D_{zz} \) is the axial component and \( D_{xx} \) and \( D_{yy} \) are the non-axial components.

It is convenient to use the functions \(|+1\rangle, |0\rangle \) and \(|-1\rangle \) as a basis set since these are
the eigenfunctions of $\mathcal{H}$. Eq.4.9 can be written in matrix form as follows:

$$\mathcal{H}_{SS} = D_{xx}S_x^2 + D_{yy}S_y^2 + D_{zz}S_z^2$$

(4.10)

Using the Pauli matrices for $S = 1$

$$S_x = \begin{pmatrix} 0 & \frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{2}} & 0 \end{pmatrix}$$  \hspace{1cm} (4.11a)

$$S_y = \begin{pmatrix} 0 & \frac{-i}{\sqrt{2}} & 0 \\ \frac{i}{\sqrt{2}} & 0 & \frac{-i}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{2}} & 0 \end{pmatrix}$$  \hspace{1cm} (4.11b)

$$S_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$  \hspace{1cm} (4.11c)

and $D_{zz} = -(D_{xx} + D_{yy})$, Eq.4.9 becomes

$$\mathcal{H}_{SS} = \begin{pmatrix} |1\rangle & |0\rangle & |-1\rangle \\ \langle 1 | & \frac{1}{2}D_{zz} & 0 & \frac{1}{2}(D_{xx} - D_{yy}) \\ \langle 0 | & 0 & -D_{zz} & 0 \\ \langle -1 | & \frac{1}{2}(D_{xx} - D_{yy}) & 0 & \frac{1}{2}D_{zz} \end{pmatrix}$$

(4.12)

By diagonalizing this Hamiltonian, we can find the corresponding eigenvalues which are the energies of this system in zero magnetic field.

$$W_x = \frac{D_{zz}}{2} - \frac{D_{xx} - D_{yy}}{2} = -D_{xx}$$  \hspace{1cm} (4.13a)

$$W_y = \frac{D_{zz}}{2} + \frac{D_{xx} - D_{yy}}{2} = -D_{yy}$$  \hspace{1cm} (4.13b)

$$W_z = -D_{zz}$$  \hspace{1cm} (4.13c)
By defining

\[ D = \frac{3D_{zz}}{2} \]  
\[ E = \frac{1}{2}(D_{xx} - D_{yy}) \]  

(4.14a, 4.14b)

Eq. 4.13 becomes

\[ W_x = \frac{1}{3}D - E \]  
\[ W_y = \frac{1}{3}D + E \]  
\[ W_z = -\frac{2}{3}D \]  

(4.15a, 4.15b, 4.15c)

The Hamiltonian Eq. 4.9 then becomes

\[ \mathcal{H}_{ss} = D(S_z^2 - \frac{1}{3}S^2) + E(S_x^2 - S_y^2) \]  

(4.16)

If we consider an NV center in strain-free diamond, we can set \( D_{xx} = D_{yy} \) because of the \( C_{3v} \) symmetry. Then the Eq. 4.16 is simply

\[ \mathcal{H}_{ss} = D(S_z^2 - \frac{1}{3}S^2) \]  

(4.17)

The experimentally observed value of \( D \) for the \( ^3A_2 \) ground state is 2.87GHz.

\( ^3E \) spin sublevels: Spin-spin interaction and spin-orbit interaction

Since \( ^3E \) state is spin triplet as well as orbital doublet, it is both affected by spin-spin interaction and spin-orbit interaction\(^{[58]}\). Since spin-spin interaction is covered in previous section, we will focus on constructing the spin-orbit Hamiltonian to understand the spin sublevels of the \( ^3E \) state.

Here we consider the interaction of the spin of each electron with its own orbital motion, namely spin-orbit interaction. It is a relativistic effect given by the relative
motion between an electron and a nucleus. This can be written in the form of

$$\mathcal{H}_{SO} = \sum_j \frac{1}{2m_e^2c^2} (\nabla V(r_j) \times p_j) \cdot s_j \quad (4.18a)$$

$$= \sum_j -\frac{E(r_j)}{2m_e^2c^2r_j} (r_j \times p_j) \cdot s_j \quad (4.18b)$$

$$= \sum_j \lambda_j L_j \cdot s_j \quad (4.18c)$$

where $L_j$ and $s_j$ is angular momentum and spin of $j$th electron ($j = 1, 2$), respectively. This can be written in an environment of $C_{3v}$ symmetry as

$$\mathcal{H}_{SO} = \lambda (L_z S_z) + \lambda' (L_x S_x + L_y S_y) \quad (4.19)$$

where $\lambda$ and $\lambda'$ are the coefficients associated with the axial and nonaxial spin-orbit interaction. Here subscript $j$ is dropped by considering only one electron for simplicity. The axial spin-orbit interaction splits the $^3E$ spin triplet into three twofold degenerate states $E$, $E'$ and an ($A_1, A_2$) pair by $\lambda$ [63, 64]. These states are written as follows.

$$E = \begin{cases} -|E_x, m_s = -1\rangle - |E_y, m_s = +1\rangle \\ -|E_x, m_s = +1\rangle + |E_y, m_s = -1\rangle \end{cases} \quad (4.20a)$$

$$E' = \begin{cases} |E_y, m_s = 0\rangle \\ |E_x, m_s = 0\rangle \end{cases} \quad (4.20b)$$

$$A_1 = |E_x, m_s = +1\rangle + |E_y, m_s = -1\rangle$$

$$A_2 = |E_x, m_s = -1\rangle - |E_y, m_s = +1\rangle \quad \text{degenerate} \quad (4.20c)$$

The non-axial spin-orbit term causes a mixing of $E$ (Eq.4.20a) and $E'$ (Eq.4.20b) states. These states possess different spin states and the mixing by the non-axial spin-orbit interaction does not conserve spin. This is very weak effect but this could result in non-100% spin polarization by optical pumping.
Since spin-orbit interaction has a Zeeman like term giving anisotropy to Landé-g factor as we will see soon, we consider the Zeeman term together with the spin-orbit term in a Hamiltonian.

\[
\mathcal{H} = \mathcal{H}_{\text{Zeeman}} + \mathcal{H}_{\text{SO}}
\]  

\[
\mathcal{H}_{\text{Zeeman}} = \mu_B \mathbf{B} \cdot (\mathbf{L} + g_e \mathbf{S}) + \lambda \mathbf{L} \cdot \mathbf{S}
\]

\[
\mathcal{H}_{\text{SO}} = g_e \mu_B \mathbf{B} \cdot \mathbf{S} + (\mu_B \mathbf{B} + \lambda \mathbf{S}) \cdot \mathbf{L}
\]

A spin-spin interaction term is not included here because it was already covered in the previous section. The orbital singlet state is considered here and is represented by \(|G, m_s\rangle\). The energy to first order is given by

\[
W^{(1)}_G = \langle G, m_s | g_e \mu_B B_z S_z | G, m_s \rangle + \langle G, m_s | (\mu_B B_z + \lambda S_z) L_z | G, m_s \rangle
\]  

Here the first term is the “spin-only” Zeeman energy. The second term is expanded as \(\langle m_s | \mu_B B_z + \lambda S_z | m'_s \rangle \langle G | L_z | G \rangle\) and \(\langle G | L_z | G \rangle = 0\) due to the fact that the orbital singlet state has zero orbital momentum as mentioned in Sec.4.5.2. Thus, we need to include the second order correction to each element in the Hamiltonian matrix to calculate the non-zero spin-orbit interaction.

\[
\mathcal{H}_{m_s,m'_s} = - \sum_n' \frac{|\langle G, m_s | (\mu_B \mathbf{B} + \lambda \mathbf{S}) \cdot \mathbf{L} + g_e \mu_B \mathbf{B} \cdot \mathbf{S} | n, m'_s \rangle|^2}{W^{(0)}_n - W^{(0)}_G}
\]

\[
= - \sum_n' \frac{[\langle m_s | (\mu_B \mathbf{B} + \lambda \mathbf{S}) | m'_s \rangle \times [\langle n | \mathbf{L} | G \rangle \cdot \langle m'_s | (\mu_B \mathbf{B} + \lambda \mathbf{S}) | m_s \rangle]}{W^{(0)}_n - W^{(0)}_G}
\]  

where the prime designates summation over all states except the ground state. The “spin only” Zeeman term in Eq.4.23a was dropped since \(\langle G | n \rangle = 0\). By defining the second-rank tensor \(\Lambda\)

\[
\Lambda = - \sum_n' \frac{\langle G | \mathbf{L} | n \rangle \langle n | \mathbf{L} | G \rangle}{W^{(0)}_n - W^{(0)}_G}
\]  

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Eq. 4.23b is reduced to

$$H_{m_s,m'_s} = \langle m_s | \mu_B^2 \mathbf{B} \cdot \mathbf{A} \cdot \mathbf{B} + 2 \lambda \mu_B \mathbf{B} \cdot \mathbf{A} \cdot \mathbf{S} + \lambda^2 \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{S} | m'_s \rangle$$  \quad (4.25)$$

Since the first term in Eq. 4.25 describes a constant contribution to the temperature independent paramagnetism\[62\], it will be ignored in this discussion. By combining Eq. 4.22 with Eq. 4.25, we can write full expression of the spin Hamiltonian as

$$H = \mu_B \mathbf{B} \cdot (g_e \mathbf{1} + 2 \lambda \mathbf{A}) \cdot \mathbf{S} + \lambda^2 \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{S}$$  \quad (4.26a)$$

$$= \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}$$  \quad (4.26b)$$

where

$$\mathbf{g} = g_e \mathbf{1} + 2 \lambda \mathbf{A}$$  \quad (4.27)$$

and

$$\mathbf{D} = \lambda^2 \mathbf{A}$$  \quad (4.28)$$

and \(\mathbf{1}\) is the unit tensor. Note that Eq. 4.26b has the same form with Eq. 4.17 except that \(\mathbf{g}\) is a tensor in the Zeeman term where the anisotropy is given by the spin-orbit interaction term.

It was, however, reported that \(\mathbf{g}\) is isotropic with the value close to 2 and zero field splitting of excited state to be just 1.42GHz at room temperature\[15, 64, 65\]. The spin-orbit splitting \(\lambda^3\) in Eq. 4.19 is not observed at room temperature. This is due to the fact that there is almost no spin-orbit contribution and the zero field splitting is only given by the spin-spin interaction. Increasing temperature is known to cause homogeneous linewidth broadening of optical transitions. This means that the lattice vibration induces transfer between electronic states and yields the standard Boltzmann distribution in the population of adjacent states. The lattice vibration is coupled to electronic orbit but not to spin. Thus, the lattice vibration causes orbital

$$^3\lambda = 5.3\text{GHz} \text{ and } \lambda' = 0.2\text{GHz}$$ was estimated from low temperature measurement\[64\].

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averaging without changing spin state. This orbital averaging quenches the spin-orbit splitting $\lambda[64, 66]$.

**Intersystem crossing and selection rule**

Now we will see how spins of NV center can be polarized and magnetic resonance is measured using optical method. The ordering of singlet states is important for understanding the optical spin polarization and magnetic resonance detection mechanism of the NV center in diamond. NV centers in diamond are known to reach more than 80% spin polarization with optical pumping[67]. This is given by the spin selective intersystem crossing (See Fig.4.6). Only the spin states of $|m_s = +1\rangle$ and $|m_s = -1\rangle$ in $^3E$ excited state have half a chance to relax through the metastable singlet state to the spin projection of $|m_s = 0\rangle$ in the $^3A_2$ ground state. This intersystem crossing is a non-radiative process and reduction of the photoluminescence is observed in this process. After several optical cycles in non-resonant condition, the NV center should be nearly 100% spin polarized in the $|m_s = 0\rangle$ spin state. With the application of the appropriate energy to match the resonance condition of this system, the $|m_s = 0\rangle$ in the $^3A_2$ ground state is manipulated to either the $|m_s = +1\rangle$ or $|m_s = -1\rangle$. Further optical pumping causes a spin conserving transition to the $^3E$ excited state and leads to 50% reduction of photoluminescence due to the non-radiative intersystem crossing described above. This is how magnetic resonance of the NV center is optically detected.

We will consider intersystem crossing in a symmetry point of view. In the first case, $^1A$ lies above $^1E$ and both states are between $^3E$ and $^3A_2$. A symmetry allowed transition is from the sublevels with $(A_1, A_2)$ symmetry in $^3E$ state to the $^1A$ state. After the electron decays from $^1A$ to $^1E$, the electron will be further relaxed from $^1E$ to the sublevels with $E$ symmetry in $^3A_2$ ground state allowed by the symmetry. In
Figure 4.6: A schematic diagram of electronic structure of NV center. The electronic structure discussed in Sec.4.5.2 is summarized with the band diagram. Zeeman splitting and hyperfine splitting are not considered here. Orbital splitting and spin-spin interaction are only considered here by restricting our discussion at room temperature. Spin-orbit interaction at room temperature is negligible. Gray boxes covering solid lines for states indicate the states are degenerate. Thick solid lines for states indicate doublet states and thin solid lines for states describe singlet state. Magenta arrows indicate light absorption (non-glowing) and emission (glowing) corresponding to electronic transitions with spin state of $|m_s = 0\rangle$. Red arrows represent photon absorption (non-glowing) and emission (glowing) corresponding to electronic transitions with spin projection of $|m_s = +1\rangle$ and $|m_s = -1\rangle$. Dotted black arrows represent non-radiative decay of the electron. Weighting of arrows implies the relative probability of electronic transitions. ‘gs’ stands for ground state and ‘es’ for excited state.
this case, there will be no change in spin polarization since spin state of \((A_1, A_2)\) levels are \(|m_s = +1\rangle\) and \(|m_s = -1\rangle\) and destination \(E\) sublevels in \(^3A_2\) possess the same spin states. In the second case, \(^1E\) state lies above \(^1A\) state and both are between the \(^3E\) excited and \(^3A_2\) ground states. A symmetry allowed transition in this case is from sublevels with symmetry \(E\) in the \(^3E\) excited states to the metastable \(^1E\) state. If transition from \(E'\) sublevel to \(^1E\) state is forbidden, only the electrons with spin states of \(|m_s = +1\rangle\) and \(|m_s = -1\rangle\) are relaxed to the \(^1E\) metastable states. After the electron decays from \(^1E\) states to \(^1A\) state, it will relax to \(A_1\) sublevel of the \(^3A_2\) states which has a spin state of \(|m_s = 0\rangle\). This process causes spins to polarize to the \(|m_s = 0\rangle\) spin state. This could be true only if transition from \(E'\) sublevel to \(^1E\) state is forbidden. A third possibility is to have only the \(^1A\) state between \(^3E\) and \(^3A_2\).

This also explains the spin polarization to the spin projection of \(|m_s = 0\rangle\) with optical pumping by having electron relax down the following path: \((A_1, A_2) \rightarrow ^1A \rightarrow A_1\).

However, this picture does not explain the observation of IR ZPL at \(1.189\text{eV}\)[68, 69]. There is no definite consensus on the ordering of singlet states for this system, but we will use the relaxation mechanism in which \(^1A\) is the only metastable state between \(^3A_2\) and \(^3E\) throughout this thesis. The electronic structure of an NV center is schematically shown by considering spin-spin interaction and orbital symmetry in Fig.4.6. Here, the spin-orbit interaction is ignored by restricting our discussion to room temperature as discussed in Sec.4.5.2. Zeeman and hyperfine splitting are also not considered in this picture.
Hyperfine interactions with NV center

Hyperfine interaction refers to the interaction of the electronic spin with the nuclear spin and is written as [70].

\[ H_{hf} = \frac{8\pi}{3} g_e g_n \mu_B \mu_n \mathbf{I} \cdot \mathbf{S} \delta(r) + \frac{g_e g_n \mu_B \mu_n}{r^3} \left[ 3 \frac{(\mathbf{I} \cdot \mathbf{r})(\mathbf{S} \cdot \mathbf{r})}{r^2} - \mathbf{I} \cdot \mathbf{S} \right] \]  

(4.29)

where \( g_e \) (\( g_n \)) is the g-factor of an electron (nucleus), \( \mu_B \) (\( \mu_n \)) is Bohr (nuclear) magneton and \( \mathbf{S} \) (\( \mathbf{I} \)) is electron (nuclear) spin. The first term, also known as the “Fermi contact” term, describes the direct interaction of the nuclear spin with the electron spin and is only nonzero for states with a finite electron spin density at the position of the nucleus (those with unpaired electrons in s-subshells). The second term relates to the finite distance interaction of the nucleus spin with the field produced by the electron spin magnetic moment and is non s-state term. Hyperfine interaction can be understood as the nuclear spin experienced by effective magnetic field generated by electron spin moment and is simply written as \( H_{hf} = B_{m_s} \cdot \mathbf{I} \).

We will now consider two types of hyperfine interaction in the NV center. First, we will consider the hyperfine interaction of the electrons with the \( ^{14}N \), and secondly, we will consider their interaction with \( ^{13}C \).

For a system with axial symmetry, such as an NV center (\( C_{3v} \)), Eq.4.4 for the ground state can be written as

\[ \mathcal{H} = D_{gs} \left( S_z^2 - \frac{S(S+1)}{3} \right) + g\mu_B \mathbf{B} \cdot \mathbf{S} + A_0 S_z I_z + A_\perp (S_x I_x + S_y I_y) + P \left( I_z^2 - \frac{I(I+1)}{3} \right) \]  

(4.30)

The first term describes zero field splitting with of the \( ^3A_3 \) ground state with \( D_{gs} = 2.87 \)GHz, and the second term is the Zeeman term. \( g \) is the electronic Landé-g factor and \( g \approx 2 \) for an NV center. The third term is axial term of the hyperfine interaction and the fourth term is non-axial term of the hyperfine interaction. The last term is
nuclear quadrupole splitting term and is valid only for $I \geq 1$ (e.g. $^{14}N$). The nuclear Zeeman splitting term is ignored since it is very weak ($g_n\mu_n = 0.307\text{kHz/G}$). $A_{\parallel}$ and $A_\perp$ are written as

$$A_{\parallel} = a + 2b$$

$$A_\perp = a - b$$

(4.31a)

(4.31b)

Here $a$ is the isotropic coefficient which comes from the Fermi contact term in Eq.4.29 and $b$ is the anisotropic coefficient which is from the non s-state term in Eq.4.29[71].

We first consider hyperfine interaction with the $^{14}N$ atom. $^{14}N$ has a nuclear spin of one. Experimentally, it has been found that $A_{\parallel} = -2.15\text{MHz}$, $A_\perp = -2.70\text{MHz}$ and $P = -5.01\text{MHz}$ and the calculated values of $a$ and $b$ from these values are $a = -2.51\text{MHz}$ and $b = 0.19\text{MHz}$[72]. Fig.4.7(a) shows the $^3A_2$ ground state energy level diagram, including hyperfine interaction with $^{14}N$, based on these values. After simple algebra using Eq.4.30, the energy level difference between $|m_s, m_I\rangle = |\pm 1, \mp 1\rangle$ and $|\pm 1, \pm 1\rangle$ is $2A_{\parallel}$. Likewise, energy difference between $|\pm 1, 0\rangle$ and $|\pm 1, \mp 1\rangle$ is $A_{\parallel} - P$ and these are depicted in Fig.4.7(a). Fig.4.7(b) shows an optically detected magnetic resonance (ODMR) spectrum of $|m_s = 0\rangle \leftrightarrow |m_s = -1\rangle$ transition under the application of 37G external field, 1.2mW laser power and -4.2dBm microwave power. The plot is inverted for better appearance. By fitting the data to three Lorentzian functions, the splittings of the hyperfine levels are found to be 2.16MHz and this agrees very well with the experimental values found in Ref.[72].

The $^{15}N$ isotope has a natural abundance of 0.1% and is a $I = 1/2$ nucleus with $g_n = -0.5664$. The hyperfine interaction with $^{15}N$ is isotropic and $A_{\parallel} = A_\perp = a = -3.05\text{MHz}$. The experimentally found value is 3.1MHz using an ODMR measurement[73].

Another hyperfine interaction to consider is the interaction of the electrons with
Figure 4.7: $^3A_2$ ground state energy level of NV center including hyperfine interaction with $^{14}N$. (a) Band diagram of ground state NV center including hyperfine interaction with $^{14}N$. $A_{ij} = -2.15$MHz and $P = -5.01$MHz[72] were used in this band diagram (b) Optically Detected Magnetic Resonance spectrum of $|m_s = 0\rangle \leftrightarrow |m_s = -1\rangle$ transition with $H = 37$G external field, 1.2mW laser power and -4.2dBm microwave power applied. The plot is inverted for better appearance. The colors of the arrows in (a) correspond to the peaks indicated with lines of the same color in (b). The data was fit to three Lorentzian functions and the splittings of hyperfine levels found from the fit are 2.16MHz. This agrees very well with the experimental values found in Ref.[72]. The full width at half max (FWHM) of each peak is 2.67MHz.
$^{13}C$. The $^{13}C$ isotope has a natural abundance of 1.1% and $I = 1/2$ nuclear spin. Due to the fact that there are many possible sites where $^{13}C$ atom could be, strength of the hyperfine interaction can largely vary. Maximum hyperfine parameters found by conventional EPR spectroscopy are $A_{||} = 199.1$MHz and $A_{\perp} = 121.1$MHz\cite{72} and this is due to the hyperfine interaction with the nearest neighboring $^{13}C$. Since there are only three sites possible for the nearest neighboring, most of the hyperfine splitting with $^{13}C$ atom are a few MHz or below.

4.6 Time scales in NV center

4.6.1 Spin lifetime

The focus of our discussion in this section is to know spin lifetimes at room temperature and corresponding relaxation mechanisms. This is done by surveying studies from other research groups.

Various research groups have measured $T_1$ of NV centers in diamond. Redman et al.\cite{16} have measured $T_1$ as a function of temperature using a conventional pulsed electron paramagnetic resonance (EPR) spectrometer and found the exponential behavior characteristics of a two-phonon Orbach process\cite{74}. The measured value at room temperature is $T_1 = 1.2$ms. On the other hand, Takahashi et al.\cite{75} have measured $T_1$ in a similar system (100-200ppm density of nitrogen impurities\footnote{1ppm = $1.76 \times 10^{17}$cm$^{-3}$ in diamond}) and found to be $T_1 = 7.7$ms. However, their data is not explained by the two-phonon Orbach process. $T_1$ at low temperature (2K) has been reported to be 10s to 100s seconds\cite{67}. The exact mechanism for the spin lattice relaxation is not yet clear.

$T_2$ of the NV center has been measured in various conditions. Takahashi et al.\cite{75} measured $T_2$ of an NV center in diamond with a high density nitrogen impurities (100-200ppm) in various temperatures using conventional pulsed EPR spectrometer.
and found that $T_2$ is independent of temperature until they fully polarize P1\textsuperscript{5} centers by a thermal polarization process. $T_2$ was found to be $7\mu s$ at room temperature down to 20K. They fully suppressed spin flip-flop process of P1 center below 1.7K and measured $T_2$ was about $250\mu s$. They concluded that the $T_2$ mechanism is dominated by electron spin bath fluctuation of nitrogen impurities. As electron spins of nitrogen impurities are frozen at high magnetic field and low temperature, $T_2$ is mainly governed by $^{13}C$ nuclear spin bath fluctuation. This was also verified by a Hahn echo measurement of ODMR in a P1 center-free diamond at room temperature. Gaebel et al.[76] created NV centers by implanting $^{14}N$ into ultra pure diamond and found $T_2 = 350\mu s$ from an individual defect. Another study also revealed that $T_2 = 50\mu s$ at room temperature[77]. This was measured from CVD grown diamond with nitrogen impurity concentration of 0.05 to 10ppm.

There are a couple of ways to increase $T_2$ of an NV center. One way is to align an external magnetic field to the NV crystal axis. The magnetic field orientation dependence of $T_2$ has been studied theoretically and experimentally. It was found that the hyperfine interaction with $^{13}C$ does not lead to decoherence when an external magnetic field is aligned to NV axis. However, if the magnetic field is misaligned to the NV axis, nuclear spins of $^{13}C$ destroy the NV center coherence. This is due to an enhancement in nuclear g-factors of $^{13}C$ nearby the NV spins leading to a position dependent Larmor frequency of the nuclei[78]. Stanwix et al.[79] found 12 times longer $T_2$ ($600\mu s$) than the values found from previous studies with about the same density of nitrogen impurities. This value is from an ensemble measurement and thus universal throughout the sample. Another way is to make the diamond isotope- and nitrogen impurity-free. $T_2$ of NV centers in an isotopically pure and nitrogen impurity free diamond was found to be $T_2 = 1.8\text{ms}$ which is about the same as the $T_1$ value of $^{5}$P1 center corresponds to electrically neutral single substitutional nitrogen atoms in the diamond lattice.

5 P1 center corresponds to electrically neutral single substitutional nitrogen atoms in the diamond lattice.
Figure 4.8: Excited state relaxation and intersystem crossing rate are summarized from Ref.[63] with the NV center electronic energy band diagram. Rates are shown in the units of $10^6 \text{s}^{-1}$. Magenta and red color depicts radiative process and black color depicts nonradiative process. Relaxation rate from $^1E$ to $^1A$ is not displayed since it is not known. Other intersystem crossing rates that are not shown here are zero.

NV centers[56].

### 4.6.2 Excited state relaxation and intersystem crossing rate

Relaxation rates from the excited state and intersystem crossing rates have been measured using single photon statistical techniques[80] and photon-echo measurements[81] and are well compiled and modeled in Ref.[63]. This is summarized in Fig.4.8 with energy band diagram.
4.7 Optically Detected Magnetic Resonance of NV centers in diamond

4.7.1 ODMR Linewidth of an ensemble of NV centers

Because one of the experiments covered in this thesis deals with the measurement of an ensemble of nitrogen-impurity centers in a diamond crystal it is worth knowing what determines the resonance linewidth of this type of measurement. For NV centers in diamond with a natural abundance of $^{13}\text{C}$ and a high concentration of nitrogen impurities (100-200ppm) at room temperature, the intrinsic relaxation time, $T_2 \approx 7\mu$s is primarily determined by the fluctuation of the electron spin bath of the nitrogen impurities as well as that of the $^{13}\text{C}$ nuclear spin bath. By solving Eq.1.1, we can easily see that the resonance linewidth can be converted to a time scale such as $\tau_s = 1/\pi b$, where $b$ is the linewidth (the full width at half max (FWHM)) of the resonance line in the ODMR spectrum. Fig.4.7(b) shows a measured hyperfine resolved linewidth of about 2.66MHz at -4.2dBm microwave power and 1.2mW optical power. This corresponds to $\tau_s = 120$ns and is about 58 times shorter than the $T_2$ value found by conventional pulse EPR spectroscopy[75]. Another thing to note is that the linewidth of an ODMR spectrum depends on angle of applied external magnetic field with respect to the NV crystal axis. Fig.4.9 shows an ODMR spectrum of an ensemble of NV centers with four different orientations (corresponding to the four crystal axes of the tetrahedral diamond structure) using -4.2dBm microwave power and 1.2mW optical power. The density of the NV and P1 centers in this measurement is 19ppm and 100ppm, respectively. We see in this data that the resonance line corresponding to one of the four NV crystal axes (titled NV4) occurs at 2870MHz and the hyperfine splitting is not resolved due to linewidth broadening. The linewidth of NV3 is slightly broader than the linewidth of NV1 and NV2 and NV4 is 1.56 times broader than
Figure 4.9: Hyperfine splitting resolved ODMR of NV centers corresponding to transition between $m_s = 0$ and $m_s = -1$. This is an ensemble measurement. 37G of magnetic field was applied to lift the degeneracy of the four different orientations of the NV crystal axes. The applied microwave power and laser power were $-4.2$dBm and 1.2mW, respectively. The diamond sample has an NV center density of 7.4ppm and a P1 center density of 100ppm. The gray line is data and the blue line is a fit of 12 Lorentzian functions. 2.15MHz of hyperfine splitting was used in the fitting functions. The linewidth corresponding to NV1, NV2, NV3 and NV4 is 2.74MHz, 2.46MHz, 2.90MHz and 4.05MHz, respectively. Broadening of the linewidth of NV4 is clearly seen and this is possibly due to a magnetic field orientation dependence of $T_2[78, 79]$.

NV1 and NV2. This seems to agree with the discussion regarding the magnetic field orientation dependence of $T_2[78, 79]$ as we discussed in Sec.4.6.1.

There are couple of other things that determine resonance linewidth other than $T_2$. First, the hyperfine interaction between the electron spins of an NV center and the nuclear spins of $^{13}C$. If $^{13}C$ is placed next to an NV center within the distance smaller than the decoupling radius $r[82]$, the nuclear spin flip-flop is strongly suppressed due to an intense hyperfine field experienced by the nucleus[76]. The decoupling radius is given by

$$r = \left[ \frac{2S\gamma_e}{\gamma_n} \right]^{1/4} a$$

where $S$ is the electron spin quantum number and $a$ is the average nearest-neighbour separation between nuclear spins. Since the $a = 0.44$nm for a natural abundance of
1.1% for $^{13}C$, $r$ becomes 2.2nm. Thus, for any $^{13}C$ that is separated from NV center by 2.2nm or less, a few of the $^{13}C$ cause a hyperfine splitting of 10s to 100s MHz, but most of them yield a hyperfine splitting of a fraction of MHz to a few MHz in ODMR. This effect would appear as a broadening of the resonance linewidth in an ensemble measurement.

Also likely, electron spins of a P1 center can cause a dipolar interaction with the NV centers and cause splitting in the resonance spectrum. In this case, the Hamiltonian can be written as

$$
\mathcal{H} = g^{NV} \mu_B B \cdot S^{NV} + D \cdot S^{NV} + g^{P1} \mu_B B \cdot S^{P1} + S^{NV} \cdot T \cdot S^{P1}
$$

(4.33)

where $g^{NV}$ and $g^{P1}$ are the Landé g factor of NV and P1 center, respectively, and have values of $g_{nv} \approx g_{p1} \approx 2$. $S^{NV}$ and $S^{P1}$ are spin matrices corresponding to NV and P1 centers, respectively. $T$ is the magnetic dipolar interaction tensor. A spin number of $S = 1/2$ of a P1 center makes each of the NV center transition from $m_s = 0$ to ±1 into a doubly degenerate states and the degeneracy is split by the dipole-dipole interaction. This splitting can be calculated using the last term of Eq.4.33. This is a position dependent splitting and has large variations. For instance, splitting of 14MHz for a defect separation distance of 1.5nm was reported[76]. This effect also could cause broadening of the resonance linewidth in ensemble measurement.

Broadening of the linewidth of a resonance spectrum by microwave power and laser power should also be considered. Microwave power have significant effect on linewidth but obvious laser power dependence of linewidth broadening was not observed. Laser power and microwave power dependence of the linewidth of a resonance spectra are shown in Fig.4.10. The linewidth of resonance line doesn’t seem to be sensitive to a laser power increase but is quite sensitive to a microwave power increase. The microwave power dependence data was fit to a linear function and the FWHM at
Figure 4.10: Optical and microwave power dependence of ODMR linewidth. (a) Optical power dependence of the ODMR linewidth. This measurement was done with a microwave power of -28dBm. Laser power was measured in the beam path right before a 100X, 1.3NA, oil immersion objective lens. No clear laser power dependence was observed. (b) The microwave power dependence of the ODMR linewidth. A laser power of 1.68mW was used for the measurements. Data was fit to linear function and the FWHM at zero microwave power was found to be 2.63MHz.

Zero microwave power was found to be 2.63MHz. Additionally, there is always a fixed hyperfine interaction with the nitrogen nuclei that make up the NV center, itself. There is a triplet degeneracy with a $^{14}N$ nuclei ($I_N = 1$) and doublet degeneracy with a $^{15}N$ nuclei ($I_N = 1/2$). The splitting is 2.15MHz for a $^{14}N$ nuclei and 3.1MHz for a $^{15}N$ nuclei as discussed in Sec.4.5.2. These have fixed splitting width but this hyperfine interaction can cause a large linewidth broadening if those splittings are not resolvable. For measurements, the linewidth can easily be broadened by microwave power and/or optical power and, each of the hyperfine splitting is no longer observable and the measured linewidth becomes about 10-12MHz. Thus it is desirable to keep the microwave power as low as possible without sacrificing signal-to-noise ratio if narrow linewidth is desired for magnetometry applications.
4.7.2 Magnetic field dependence of ODMR

In order to focus on the magnetic field dependence of spin behavior of the NV centers in their ground state, we will ignore the hyperfine interaction in the spin Hamiltonian (Eq.4.30).

\[
\mathcal{H} = D_{gs} \left( S_z^2 - \frac{S(S+1)}{3} \right) + g\mu_B \mathbf{B} \cdot \mathbf{S} \tag{4.34a}
\]

\[
= D_{gs} \left( S_z^2 - \frac{2}{3} \right) + g\mu_B (B_x S_x + B_y S_y + B_z S_z) \tag{4.34b}
\]

This can be rewritten in matrix form using the following relations

\[
S_x = \frac{S_+ + S_-}{2} \tag{4.35a}
\]

\[
S_y = \frac{S_+ - S_-}{2i} \tag{4.35b}
\]

\[
S_+ |m_s\rangle = \sqrt{(s + m_s + 1)(s - m_s)} |m_s + 1\rangle \tag{4.35c}
\]

\[
S_- |m_s\rangle = \sqrt{(s + m_s)(s - m_s + 1)} |m_s - 1\rangle \tag{4.35d}
\]

and magnetic field components in spherical coordinate as

\[
B_x = B_0 \sin \theta \cos \phi = B_0 \sin \theta \tag{4.36a}
\]

\[
B_y = B_0 \sin \theta \sin \phi = 0 \tag{4.36b}
\]

\[
B_z = B_0 \cos \theta \tag{4.36c}
\]

Here \(\phi = 0\) is given by \(C_{3v}\) symmetry around [111] axis which is in parallel with \(\hat{z}\) direction. Then,

\[
\mathcal{H} \Psi = \begin{bmatrix}
\frac{1}{3} D_{gs} + g\mu_B B_0 \cos \theta & g\mu_B \frac{B_0 \sin \theta}{\sqrt{2}} & 0 \\
g\mu_B \frac{B_0 \sin \theta}{\sqrt{2}} & -\frac{2}{3} D_{gs} & g\mu_B \frac{B_0 \sin \theta}{\sqrt{2}} \\
0 & g\mu_B \frac{B_0 \sin \theta}{\sqrt{2}} & \frac{1}{3} D_{gs} - g\mu_B B_0 \cos \theta
\end{bmatrix} \begin{bmatrix}
|1\rangle \\
|0\rangle \\
| -1 \rangle
\end{bmatrix} \tag{4.37}
\]
The analytical solution of Eq. 4.37 as a function of external magnetic field at $0^\circ$ and $51.9^\circ$ are plotted in Fig.4.11(a). The dotted line represents $\theta = 0^\circ$ and solid line represents $\theta = 51.9^\circ$. The red, orange and blue lines correspond to $|m_s = 1\rangle$, $|m_s = -1\rangle$ and $|m_s = 0\rangle$ states, respectively. The solutions for $\theta = 0^\circ$ show that a level anti-crossing (LAC) occurs between $|m_s = 0\rangle$ and $|m_s = -1\rangle$ at about 1,030G. The gap between $|m_s - 1\rangle$ and $|m_s = 0\rangle$ gets broader as the angle $\theta$ gets bigger and the LAC eventually disappears after $\theta$ of a few degrees[83]. Another thing to note is that spin states are mixed by the magnetic field $B$ for non-zero angle between $B$ and $[111]$. For instance, $|m_s = 0\rangle$ becomes $g\mu_B \frac{B_0}{\sqrt{2}} \sin \theta |1\rangle - \frac{2}{3} D_{gs} |0\rangle + g\mu_B \frac{B_0}{\sqrt{2}} |-1\rangle$ in the presence of magnetic field. This means that $|1\rangle$ and $|-1\rangle$ starts to mix into the $|0\rangle$ for nonzero $\theta$. That is why we see that the solution for $51.9^\circ$ in Fig.4.11(a) is no longer linear and this causes the disappearance of LAC. Fig.4.11(b) shows the ODMR peak splittings as a function of magnetic field for transitions of $|0\rangle \rightarrow |1\rangle$ (red curves) and $|0\rangle \rightarrow |-1\rangle$ (blue curves) for two different angles $\theta = 0^\circ$ (dotted lines), 51.9° (solid curves). Slopes of the ODMR peak shifts as a function magnetic field gets smaller as the angle becomes bigger and this is more significant for transition of $|0\rangle \rightarrow |-1\rangle$ especially in the small field regime. Magnetic field amplitude and angle dependence of the peak splittings are shown in Fig.4.12. Fig.4.12(a) shows the peak splitting in the field range from 0 to 1,500G and (b) in the field range from 0 to 100G.

Fig.4.13 shows an actual measurement of ODMR as a function of magnetic field. Details regarding the measurement setup are discussed in Chapter 5. Uniform magnetic field was applied to a bulk diamond and ODMR of a single NV center was measured using a home-built confocal microscope. Fig.4.13(a) shows a series of ODMR spectra as a function of magnetic field. The ODMR spectra were inverted for a better appearance. It is clear that the separation of the two peaks increases as the amplitude of external magnetic field is swept from 0G to 100G. The ODMR spectra in
Figure 4.11: Magnetic field dependence of NV center electron spin sublevels and corresponding ODMR peak splitting in the $^3A_2$ ground state. (a) The magnetic field dependence of the NV center electron spin sublevels in the $^3A_2$ ground state. Dotted lines are for $\theta = 0^\circ$ and solid lines are for $\theta = 51.9^\circ$. Here $\theta$ is angle between external magnetic field orientation and NV center crystal axis. Red, orange and blue lines correspond to $|m_s = 1\rangle$, $|m_s = -1\rangle$ and $|m_s = 0\rangle$ states, respectively. (b) The corresponding ODMR peak positions as a function of magnetic field. The red line is for transition of $|0\rangle \rightarrow |+1\rangle$ and the blue line is for transition of $|0\rangle \rightarrow |-1\rangle$.

Figure 4.12: Magnetic field amplitude and angle dependence of the ODMR peak splitting. (a) The peak splittings in the field range from 0 to 1,500G. (b) The peak splittings in the field range from 0 to 100G.
Figure 4.13: Magnetic field dependence of ODMR spectra of a single NV center. 2.14mW of laser power and 20dBm of microwave power were applied for this measurement. Single crystal synthesized diamond with 200ppm nitrogen impurities (Element-6) are used for the measurement. The NV centers were naturally created during High Pressure High Temperature (HPHT) process. (a) A series of ODMR spectra as a function of uniform magnetic field. (b) Peak positions of the ODMR spectra as a function of magnetic field. Peak positions (dots) are found by fitting the spectra to two Lorentzian functions in (a) and each branch is fit to Eq.4.37 (solid lines). Red corresponds to transition of $|0\rangle \rightarrow |1\rangle$ and blue corresponds to transition of $|0\rangle \rightarrow |{-1}\rangle$. $\theta = 51.9^\circ$ is found from the fit.

Fig.4.13(a) were fit to two Lorentzian functions except the spectrum for 0G. The spectrum for 0G was fit to a single Lorentzian function. Peak points found from the Lorentzian fits are plotted with dots in Fig.4.13(b) and solid lines are fit to Eq.4.37. From the fit, the angle of the applied magnetic field with respect to the NV crystal axis, $\theta$, is found to be $51.9^\circ$. 


Chapter 5
DEVELOPMENT OF SCANNING NV CENTER MAGNETOMETRY

In this chapter, the fringing magnetic field of a thin film magnetic microstructure is imaged using NV centers in a bulk diamond. First, we discuss how to create and characterize high density NV centers in bulk diamond. Then, a detailed experimental setup to measure optically detected magnetic resonance (ODMR) is described. Finally, scanning vector field imaging of a micron sized magnetic zigzag wire using NV centers in the diamond is discussed.

5.1 Creation of NV centers in bulk diamond

Here we study NV centers in bulk diamond. Since the density of NV centers in synthesized diamond is not sufficient enough to develop scanning vector field magnetometry, we increased density of NV centers using a diamond irradiation technique.

5.1.1 Irradiation and annealing of diamond

Synthetic bulk diamonds were purchased from Sumitomo and Element-6. These are fabricated using a high pressure high temperature (HPHT) process or a chemical vapor deposition (CVD) technique. Type Ib diamond and type IIa were used to prepare NV centers. Type Ib refers to a synthetic single crystal diamond containing evenly dis-
tributed nitrogen impurities with a density of several tens of ppm. 1ppm for diamond corresponds to $1.76 \times 10^{17} \text{cm}^{-3}$. Type Ib diamonds from Sumitomo and Element-6 contain about 100ppm and 200ppm nitrogen impurities, respectively. The color of these diamonds is yellow because of the high density of P1 centers. A P1 center is the term used in electron paramagnetic resonance (EPR) spectroscopy and indicates nitrogen impurities in diamond crystal. A CVD grown diamond from Element-6 is type IIa and has less than 1ppm of nitrogen impurities. Next, all of these diamonds were irradiated using 1.5MeV electrons at Prism Gem, LLC with various dosages. The target substrate was water-cooled to keep the temperature of the diamonds under $126^\circ \text{C}$ to avoid surface oxidation and vacancy carbon recombinations[84]. The actual temperature at the diamond pieces was estimated to be 315-370°C. We used three different electron dosages: $3.48 \times 10^{18} \text{cm}^{-2}$, $6.96 \times 10^{18} \text{cm}^{-2}$ and $1.04 \times 10^{19} \text{cm}^{-2}$ for the Sumitomo diamonds and $1.04 \times 10^{19} \text{cm}^{-2}$ only for the Element-6 diamonds. The electron irradiation turns the color of the diamonds to deep greenish blue which is caused by vacancy defect centers. The vacancy production rate is estimated to be about $1 \text{ vacancy/e}^-/\text{cm}$ based on Ref.[84, 85]. Concentration of vacancies are calculated for each dosage using the vacancy production rate and estimated to be 19ppm, 38ppm and 59ppm for $3.48 \times 10^{18} \text{cm}^{-2}$, $6.96 \times 10^{18} \text{cm}^{-2}$ and $1.04 \times 10^{19} \text{cm}^{-2}$, respectively. After the electron irradiation, Fourier transform infrared (FTIR) spectroscopy was used to compare the diamonds pre- and post-irradiation which is discussed in Sec.5.1.2. After irradiation, the diamonds were thermally annealed by K. Wickey in Prof. Johnston-Halperin’s lab. The annealing was done at $950^\circ \text{C}$ for two hours in a forming gas (N$_2$ : O$_2$ = 95 : 5) environment. Forming gas was used to prevent any surface oxidation of the diamonds. After the annealing process was completed, conventional electron paramagnetic resonance spectroscopy was used to measure density of NV centers in the diamonds and this is discussed in Sec.5.1.2. Fig.5.1 shows change
in colors of the diamonds after each step of the process.

5.1.2 Characterization of NV center enriched diamond

Because only the Sumitomo diamonds were irradiated with various dosages, I mainly focus on the characterization of these diamonds using Fourier transform infrared (FTIR) spectroscopy and conventional electron paramagnetic resonance (EPR) spectroscopy in this section.

Infrared absorption study

The diamonds, both before and after the e-beam irradiation, were characterized by diffusion reflectance infrared Fourier transform spectroscopy (DRIFTS) (Alpha, Bruker optics). DRIFTs is easy to use but quantitative analysis is not trivial. Fig.5.2 shows comparison of diamonds with various electron dosages. Four different electron beam irradiation conditions are compared here. ‘sumi2 as-is’ indicates spectrum of Sumitomo diamond before irradiation. ‘sumi1 irradiated’, ‘sumi2 irradiated’ and ‘sumi3 irradiated’ correspond to FTIR spectra of Sumitomo diamonds with irradiation conditions of $3.48 \times 10^{18} \text{cm}^{-2}$, $6.96 \times 10^{18} \text{cm}^{-2}$ and $1.04 \times 10^{19} \text{cm}^{-2}$, respectively. The X center is at a wavenumber of 1332cm$^{-2}$ and indicates one phonon absorption of a positively charged single substitutional nitrogen atom[86]. This grows proportionally with increase of NV centers since NV centers are acceptors of the donated electrons from nitrogen atoms. Thus, this is a good indication that more negatively charged NV centers are produced by higher dosages of electrons. Increase of vacancies due to higher dosages implies a higher chance to form NV centers with nitrogen atoms since vacancies becomes a bit mobile due to heating during the irradiation process. The C center at 1130cm$^{-2}$ is an absorption line induced by single substitutional nitrogen atoms. Its EPR analogy is the P1 center. One can see that the C center is suppressed
Figure 5.1: Changes in colors of diamonds after e-beam irradiation and thermal annealing. (a) Changes in colors of Sumitomo diamonds before and after irradiation and annealing process. (b) Changes in colors of Element-6 diamonds before and after irradiation and annealing process. Electron dosage of $1.04 \times 10^{19}\text{cm}^{-2}$ was used for both a HPHT type 1b and a CVD type IIa diamonds.
as more of NV centers are formed by higher electron dosages. Peaks near 1533 cm$^{-2}$ only appear in irradiated diamond. These peaks are due to nitrogen interstitial atoms surrounded by carbon atoms and will disappear after annealing. Peaks at 1045 cm$^{-1}$ and 945 cm$^{-1}$ are subpeaks of the X center.

**Conventional electron paramagnetic resonance study**

After the diamonds were annealed, a conventional cw-electron paramagnetic resonance (EPR) spectrometer (EMX plus, Bruker BioSpin) was used to measure the density of NV centers in the diamonds. Since density of P1 centers of the diamonds is known to be 100 ppm (Sumitomo and [83]), we used this value as our calibration factor and measured the density of the NV centers from the EPR lines of P1 centers and NV centers. All the measurements by conventional cw-EPR measurement were performed without optical pumping. We measured the EPR spectra of the diamonds at 9.723 GHz with a microwave power of $6.33 \times 10^{-2}$ mW. Fig.5.3 shows the raw data of the EPR spectrum of the Sumitomo diamond irradiated with 1.5 MeV electrons with a dose of $6.96 \times 10^{18}$ cm$^{-2}$ and subsequently annealed at 925°C for two hours. An external magnetic field was applied and the direction of the magnetic field was slightly misaligned from [110] by about 8°. This misalignment serves to lift the degeneracy of the NV center EPR lines between different crystal axes. EPR lines found in the magnetic field range between 3420 G and 3510 G correspond to P1 centers. Since P1 centers have an electron spin of $S = 1/2$ and a nuclear spin of $I = 1$ ($^{14}$N), its triplet degeneracy is lifted by a hyperfine interaction. The energy diagram in Fig.5.4(a) explains the three EPR lines given by this hyperfine interaction. Given that the direction of the applied magnetic field is [110] and the four possible P1 crystal axes are given by its tetrahedral structure, we can understand these EPR lines for the P1
Figure 5.2: Fourier transform infrared (FTIR) measurements of irradiated diamonds. Four different electron beam irradiation conditions are compared. ‘sumi2 as-is’ indicates the spectrum of a Sumitomo diamond before irradiation. ‘sumi1 irradiated’, ‘sumi2 irradiated’ and ‘sumi3 irradiated’ correspond to FTIR spectra of Sumitomo diamonds after an electron irradiation with a dose of $3.48 \times 10^{18}\text{cm}^{-2}$, $6.96 \times 10^{18}\text{cm}^{-2}$ and $1.04 \times 10^{19}\text{cm}^{-2}$, respectively. The X center is at wavenumber of $1332\text{cm}^{-2}$ and indicates an one phonon absorption of positively charged single substitutional nitrogen atom. The C center at $1130\text{cm}^{-2}$ is an absorption line induced by single substitutional nitrogen atoms. Peaks near $1533\text{cm}^{-2}$ only appear in irradiated diamond. These peaks are due to a nitrogen interstitial atom surrounded by carbon atoms and will disappear after annealing. The measurements were done by Prism Gem, LLC.
centers. The EPR lines of the P1 centers can be described by the spin Hamiltonian

\[ \mathcal{H}^{P1} = \mu_B \mathbf{S}^{P1} \cdot \mathbf{g}^{P1} \cdot \mathbf{B} + A^{P1}_\parallel S^z I_z + A^{P1}_\perp (S^x I_x + S^y I_y) \]  \hspace{1cm} (5.1)

where \( \mathbf{g}^{P1} \) is a slightly anisotropic g-tensor and its value is close to 2. Hyperfine splitting, \( |K| \), depends on the angle and is given by\[^{[87]}\]

\[ |K| = \sqrt{(A^{P1}_\parallel)^2 \cos^2 \theta + (A^{P1}_\perp)^2 \sin^2 \theta} \]  \hspace{1cm} (5.2)

where \( \theta \) is the angle between a P1 crystal axis and magnetic field orientation and 
\( A^{P1}_\parallel = 114.24\text{MHz}(40.8\text{G}) \) and \( A^{P1}_\perp = 81.76\text{MHz}(29.2\text{G}) \)[87]. For the case of a magnetic field parallel to [110], the EPR lines for [111] and [\bar{1}11] are degenerate and the EPR lines for [\bar{1}1\bar{1}] and [1\bar{1}\bar{1}] are degenerate as well. The splitting of the peaks for [111] and [\bar{1}11] should be -37.4G and and the splitting for [\bar{1}1\bar{1}] and [1\bar{1}\bar{1}] should be 29.2G and this matches the EPR spectrum in Fig.5.3. Slight discrepancy of the values of the hyperfine splitting is due to the 8° misalignment. The intensity of the center peak is caused by four fold degeneracy of the four crystal axes. The hyperfine interaction splits the signal of one electron spin into three peaks. In order to calculate the number of spins of one of the crystal axes, the area under the curve (AUC) of the absorption peak for the transition of \(|m_s = -1/2, m_I = 0\rangle \leftrightarrow |m_s = 1/2, m_I = 0\rangle\) should be multiplied by 3/4.

We found other EPR lines around 3776G that demonstrated a poor signal-to-noise ratio (see Fig.5.3). This is an EPR line of the NV centers along one crystal axis. Fig.5.4(b) shows the energy diagram of an NV center. Although NV centers also experience a hyperfine interaction with their own \(^{14}\text{N}\), its splitting is too small to be resolved by the EPR spectrometer as \( A^{NV}_\parallel = 2.15\text{MHz} \text{ (0.77G)} \) and \( A^{NV}_\perp = -2.70\text{MHz} \text{ (0.96G)} \) and we only see transitions as shown in Fig.5.4(b). Due to a slight misalignment of the orientation of a magnetic field with respect to [110] direction.
(~ 8°), the degeneracy of EPR lines for [111] and [111] is lifted. However, we see only one EPR line in Fig.5.3. The EPR signal from one axis is split into two lines since there are two possible transitions, $|m_s = -1\rangle \leftrightarrow |m_s = 0\rangle$ and $|m_s = 0\rangle \leftrightarrow |m_s = 1\rangle$. The EPR lines for $m_s = |0\rangle \leftrightarrow |m_s = 1\rangle$ are much lower in magnetic field (below 1500G) and are not included in the spectrum (Fig.5.3). Thus, The AUC of the absorption curve should be multiplied by two to calculate the signal coming from [111] axis NV centers only. Fig.5.5 shows absorption peaks of P1 and NV centers which were obtained by integration of spectrum shown in Fig.5.3. Thus density of NV centers can be calculated by

$$n^{NV} = n^{P1} \times \frac{\text{AUC of NV absorption curve} \times 2}{\text{AUC of P1 absorption curve} \times \frac{3}{4}} \quad (5.3)$$

The AUC of P1 centers from the untreated Sumitomo diamond is 722 and the AUC of the NV centers from the electron irradiated Sumitomo diamond with a dose of 6.96 × 10^{18}cm^{-2} is 15. Since $n^{P1}$ is 100ppm, the density of NV centers in the sample is calculated to be 5.5ppm.

Now we will use this sample as a calibration sample to measure the density of the NV centers of the other diamond pieces using our home-built confocal microscope. For instance, the estimated density of NV centers of the electron irradiated Sumitomo diamond with a dose of 1.04 × 10^{19}cm^{-2} is 19ppm. The densities of NV centers found in our samples with the given density of nitrogen impurities and vacancies are in good agreement with values found in Ref.[88].

### 5.2 Experimental setup

#### 5.2.1 Optical setup

In order to measure ODMR of NV centers in diamond, a home-built confocal microscope was set up. A schematic diagram of this microscope is shown in Fig.5.6. A
Figure 5.3: Conventional electron paramagnetic resonance measurement of P1 centers and NV centers. Magnetic field is applied along [110] direction with slight misalignment by 8°. Thus only one crystal axis of NV center for transition $|m_s = 0\rangle \leftrightarrow |m_s = -1\rangle$ appears in the spectrum.
Figure 5.4: Energy diagram of a P1 and a NV center. (a) Energy diagram of a P1 center. Triplet degeneracy is lifted by hyperfine interaction. Hyperfine splitting is given by

\[ K = \sqrt{(A_{P1}^\parallel)^2 \cos^2 \theta + (A_{P1}^\perp)^2 \sin^2 \theta} \]

where \( A_{P1}^\parallel \) is 114.24MHz (40.8G) and \( A_{P1}^\perp \) is 81.76MHz (29.2G)[87]. (b) Energy diagram of a NV center. Hyperfine splitting is given by \( A_{NV}^\parallel = -2.15MHz \) and \( A_{NV}^\perp = -2.70MHz \)[72]. Hyperfine splittings of NV centers in conventional EPR measurement are not resolvable and only resonance lines for two transitions appear in a spectrum.

Figure 5.5: Absorption spectra of EPR of P1 centers and NV centers. They are obtained by integrating spectrum in Fig.5.3. Dots are data and solid lines are fit to Lorentzian function. Areas under the curve are calculated from the fits.
A diode-pumped solid state (DPSS) laser emitting at 532nm was used to excite NV centers with a maximum power of 250mW. A strong 532nm laser is generated by doubling frequency of 1064nm, which is produced by pumping Nd:YAG with 808nm GaAlAs laser diode. Due to the mechanism of creating the 532nm laser, 532nm photons are slightly contaminated by 808nm and 1064nm photons, which could be a serious source of background noise. To eliminate the photons of unwanted wavelength, a band pass filter (FF01-531/22-25, Semrock) was used. The beam diameter is increased by a pair of lenses, which serves as a telescope. The expanded pump beam fills up back aperture of a 100X objective lens with the numerical aperture (NA) of 1.3 (CFI Plan Fluor 100X, Nikon) in order to achieve diffraction-limited spot size on the sample. Diffraction limited spot size for infinity corrected objective lens can be calculated by [89]

\[ d_\infty = 1.22 \lambda_{\text{pump}} \left[ \left( \frac{n_0}{\text{NA}} \right)^2 - 1 \right]^{1/2} \]  

(5.4)

where \( n_0 \) is the index of refraction of a medium where the beam is focused and \( \lambda_{\text{pump}} \) is the wavelength of the pump beam. Using NA=1.3 for our objective lens, \( n_0 = 1.517 \) and \( \lambda_{\text{pump}} = 532\text{nm} \), a spot size of \( d_\infty = 390\text{nm} \) is obtained. Measured beam spot size is about 430nm and is close to the theoretical diffraction limited spot size. The pump beam is reflected and directed toward the sample by a dichroic mirror (Z532RDC, Chroma), which reflects 532nm light and transmits all other wavelengths. This is an important optical component since we use the same objective lens to focus the pump beam for excitation and to collect photoluminescence (PL). Because there is such strong reflected and scattered pump light collected back at the dichroic mirror, not all the 532nm pump light is filtered out by the dichroic mirror. Thus we used a 532nm notch filter (NF03-532/1064E-25, Semrock) to remove any 532nm pump light which survived after passing through the dichroic mirror. After the notch filter, half of the PL goes to a camera for wide-field imaging and position feedback. The other
half goes through a pinhole (900PH series, Newport) to block all the out-of-focus light. The diameter of the pinhole is determined by the magnification factor $M$ and a wavelength of detected photons $\lambda_{PL}$

$$d_{\text{pinhole}} = d_{\infty} M \frac{\lambda_{PL}}{\lambda_{\text{pump}}}$$  \hspace{1cm} (5.5)

The effective focal length of the objective lens in our setup is $f_o = 2$mm and the focal length of an imaging lens before the pinhole is $f_i = 75$mm. Thus magnification is $M = f_i / f_o = 37.5$. For $\lambda_{PL} = 800$nm, a pinhole size of $d_{\text{pinhole}} = 22 \mu$m is obtained. A pinhole with a size of $20 \mu$m was used in this experiment. The position of the pinhole is adjusted by $x$, $y$ and $z$ manual stages. Then the PL from the sample is collected by either a home-built avalanche photodiode (APD) module or a spectrometer with a LN cooled CCD (Spec-10:256/ST133B, Princeton instruments). The beam path for each detector is controlled by a mirror on a flip mount. The home-built APD is protected by a long pass filter (HQ620LP, Chroma) to remove all unwanted light below $\lambda = 620$nm. The home-built APD module was made using a ball lens integrated avalanche photodiode (AD500-8-S1 BL, Pacific Silicon Sensor) mounted on a thermoelectric cooler (TEC) (TCLDM9, Thorlabs). The temperature is kept at $0^\circ$C using a temperature controller (TED200C, Thorlabs) to minimize dark current below 100pA and 152V bias voltage is applied to achieve an optical gain of 100 using a voltage source meter (2410, Keithley). Optical gain of 100 was chosen since the signal-to-noise ratio is maximized around this optical gain. A lock-in amplifier (7265, Signal Recovery) is used to demodulate the microwave amplitude modulated signal of PL from NV centers in a diamond. A typical ODMR spectrum is obtained by sweeping microwave frequencies.
Figure 5.6: Schematic diagram of home-built confocal microscope for ODMR measurement of NV center in diamond. A laser emitting at 532nm is focused onto the diamond surface by a 100X 1.3NA oil immersion objective lens and photoluminescence is collected by the same lens and measured by a home-built avalanche photodiode module.

5.2.2 Coplanar waveguide fabrication

In order to sweep the microwave frequency without the frequency dependent loss of microwave power for magnetic resonance experiment, a broadband coplanar waveguide (CPW) was fabricated on a borosilicate glass coverslip. Most of the glass coverslip has enough defects and impurities like iron to give PL that could act as a source of noise. Thus borosilicate glass coverslip (D263M, Fisher-Scientific) is designed to be used for fluorescence microscope by significantly reducing iron content. Its index of refraction is 1.523 which is suitable for a microscope with an oil immersion lens to achieve diffraction-limited spatial resolution. Fig.5.7(a) shows PL spectra of regular glass coverslip, borosilicate glass coverslip and quartz coverslip. The quartz coverslip shows excellent optical properties, making it suitable as a substrate for fluorescence
measurement but has a mismatch of index of refraction (1.46) with the immersion oil (1.517). Thus borosilicate glass coverslip was used as a substrate of the CPW in our experiment. The CPW has a gap of 0.25mm between the center stripline and the ground plane and a laser beam is focused on a diamond surface through the gap. The CPW is fabricated using standard photolithography and lift-off process. Copper film was deposited by an e-beam evaporation technique and its thickness is 70-80nm. After the CPW is fabricated, transmission of microwave power through the CPW was tested using a vector network analyser (37269C, Anritsu). Fig.5.7(b) shows a picture of the CPW mounted on a waveguide holder and microwave transmission spectrum as a function of microwave frequency. S12 indicates microwave power loss when microwaves propagate from port 1 to port 2. It shows only 5dB loss of microwave power by the CPW and the power loss is independent of microwave frequency above 2GHz.

5.2.3 Zigzag wire fabrication

A. Hauser in Prof. Fengyang’s lab deposited 20nm-thick Co$_{0.5}$Fe$_{0.5}$ film using a sputtering deposition system and G. Vieira in Prof. Sooryakumar’s lab fabricated CoFe zigzag wires on the surface of NV center enriched bulk diamond using e-beam lithography and lift-off process. The width of the zigzag wire is about 1µm. A schematic diagram of how the bulk diamond is glued on the CPW and micrograph of zigzag wires fabricated on the surface of a diamond, which are glued on the CPW, are shown in Fig.5.8.
Figure 5.7: Characteristics of coplanar waveguide (CPW) used in this experiment. (a) Optical spectra of various coverslip. Green, red and blue curves are PL measured from regular glass, borosilicate glass and quartz coverslip, respectively. Borosilicate glass coverslip is used as a substrate of CPW in this experiment. (b) S12 and S21 of CPW and picture of the waveguide holder. It shows broadband 5dB loss only from 2GHz upto 5GHz or higher.

5.3 Vector field imaging of zigzag wire

5.3.1 Motivation

Techniques of precise manipulation to probe, sort, or assemble cells down to the level of single molecules have been improved in recent years. Example include optical tweezers, magnetic tweezers and atomic force microscopy[90, 91]. Although these techniques have been proven to have many advantages including high accuracy, they also have drawbacks such as photo-damage, lack of manipulation ability, etc. Recently, Vieira et al. [92] have demonstrated that a highly localized magnetic field gradient created at the vertices of ferromagnetic zigzag wires can be utilized to manipulate individual or multiple T-lymphocyte cells attached to magnetic microspheres with high speed and accuracy but without any damage. We explored imaging spatially
Figure 5.8: Sample structure of zigzag CoFe wires on a diamond surface. (a) A schematic diagram showing how a NV center enriched diamond is mounted on a CPW (b) Micrograph of zigzag wires fabricated on the surface of the NV center enriched diamond. Part of the CPW is also shown since the micrograph is taken through the CPW substrate. The diamond appears to be pink showing abundance of NV centers. The density of NV centers in this diamond sample is 5.5ppm.
varying magnetic field vectors above the vertices of the wires in order to understand the mechanism of the magnetic wire trap manipulation. NV centers in diamond were used as a high sensitivity, high spatial resolution scanning vector magnetometry sensor by measuring the variation of the ODMR signal using our home-built confocal microscope at ambient conditions. Exploiting the electron spin resonance (ESR) shifts of the 4 different crystal axes of the NV centers given by the tetrahedral structure of diamond, which is determined by the magnitude and the orientation of the magnetic field with respect to each axis of the NV centers, the magnetic fields $x$, $y$, and $z$ components can be uniquely determined and spatially mapped out.

5.3.2 Observation of magnetic domain on zigzag wire

Prior to all measurements, a magnetic field of more than 1 tesla is applied to magnetize the zigzag wires into the desired configuration. This magnetization creates a magnetic domain wall at the vertices of the zigzag wires\cite{92} and its associated field $H_{DW}$ traps a magnetic particle. Magnetization configuration of the zigzag wire is shown in Fig.5.9. Magnetic domain structure of the zigzag wire, which was fabricated on the surface of a diamond, was then investigated using magnetic force microscopy (MFM). An MFM image, which was taken at a lift height of 70nm using a cantilever with low magnetic moment tip, is shown in Fig.5.10(a). This clearly shows that magnetic domain walls are formed at the vertices of the zigzag wire. Higher resolution of magnetic force image was obtained by scanning at a lift height of 40nm and shows a much clearer picture of the domain wall in Fig.5.10(b).

5.3.3 Vector field simulation

In order to predict how the fringing magnetic field from the vertex of the zigzag wire should look, we used OOMMF (Object Oriented Micromagnetic Framework,
Figure 5.9: Schematic of magnetization configuration of a zigzag wire with a head-to-head (HH) domain wall (DW) at the vertex. This domain wall is associated with the field $H_{DW}$, which traps a magnetic particle (gray circle). The diagram was taken from Ref.[92].

Figure 5.10: Magnetic force images of domain walls at vertices of a zigzag wire, which is fabricated on the surface of a diamond. (a) is low resolution MFM images at lift height of 70nm. (b) is high resolution MFM images at lift height of 40nm taken from area with dotted circle in (a).
NIST) and Matlab (Mathworks) as simulation tools. In order to define the geometry of the magnetic structure, we used an MFM image taken by a SmCo high moment tip. Magnetic force imaging using the high moment tip does not reveal the domain structure due to the fact that it fully magnetizes the zigzag wire out-of-plane. This, however, separates topography of magnetic materials from nonmagnetic materials. It is not trivial to get topography of magnetic materials only using atomic force microscope (AFM) or scanning electron microscope (SEM) if the surface of the sample is contaminated or has residues from fabrication. The MFM image taken by the high moment tip was used to calculate the most efficient magnetic alignment by OOMMF. Interaction between magnetic moments in nanometer scale is described by the Landau-Lifshitz-Gilbert equation\[93, 94\]

$$\frac{\partial \mathbf{M}}{\partial t} = -\gamma \mathbf{M} \times \mathbf{B}_{\text{eff}} - \frac{\gamma \alpha}{M_s} \mathbf{M} \times (\mathbf{M} \times \mathbf{B}_{\text{eff}})$$  \hspace{1cm} (5.6)

where \(\mathbf{M}\) is the magnetization, \(\mathbf{B}_{\text{eff}}\) is the effective magnetic field. \(\alpha\) is the Gilbert phenomenological damping parameter, \(\gamma\) is the electron gyromagnetic ratio, and \(M_s\) is the saturation magnetization. The effective field \(B_{\text{eff}}\) is defined as

$$B_{\text{eff}} = -\frac{2}{\mu_0 M_s} \nabla \cdot (A \nabla \mathbf{m}) - \frac{1}{\mu_0 M_s} \frac{\partial F_{\text{an}}(\mathbf{m})}{\partial \mathbf{m}} + \mathbf{B}_{\text{demag}} + \mathbf{B}_{\text{ext}}$$  \hspace{1cm} (5.7a)

$$= -\mu_0^{-1} \frac{\partial E}{\partial \mathbf{M}}$$  \hspace{1cm} (5.7b)

where each terms correspond to exchange interaction, crystalline anisotropy interaction, demagnetization field and Zeeman field, respectively. \(E\) is the average energy density, which is a function of \(\mathbf{M}\). Here \(A\) is the exchange stiffness constant. \(F_{\text{an}}(\mathbf{m}) = K_0 + K_1 \sin^2 \theta\) where \(K_1\) is the crystalline anisotropic constant. OOMMF solves Eq.5.6 iteratively to obtain the equilibrium configuration of \(\mathbf{M}\) by minimizing the total energy of the system. Parameters used for the OOMMF calculation is as follows: \(M_s = 1910 \times 10^3 \text{A/m}[95]\), \(A = 17.5 \times 10^{-12} \text{J/m}[96]\), \(K_1 = -1 \times 10^4 \text{J/m}^3[97]\),
Thickness of CoFe=20nm, Width of the wire=1µm, external field \( \{B_x = 30.62\text{G}; B_y = -18.22\text{G}; B_z = 44.92\text{G}\} \) and the cell size=26nm.

The fringing field at position \((x,y)\) is determined by summing dipole fields from all the magnetic moments in the zigzag wire. Each magnetic field vector was averaged over confocal volume of the microscope. The calculated configurations of the magnetization of the zigzag wire and its fringing fields are shown in Fig.5.11 for several different probe-sample distances. For the probe-sample distance of 2.2µm, for instance, maximum magnitude of the vector field near the vertex of the zigzag wire is about 5G.

5.3.4 Vector field imaging using NV centers

ODMR measurement was achieved by applying magnetic field of \( B_x = 30.62\text{G}, B_y = -18.22\text{G} \) and \( B_z = 44.92\text{G} \). These field components were measured by a gaussmeter at the focal point of the 532nm laser. As seen in Fig.5.12, the angle between \([100]\) of the diamond (along the edge of the diamond) and \(\hat{x}\) axis is about 59° and magnetic field components along \([100]\), \([010]\) and \([001]\) are converted to be \(B_{[100]} = 31.39\text{G}, B_{[010]} = -16.86\text{G} \) and \(B_{[001]} = 44.92\text{G} \). Applying such an external magnetic field is important for two reasons. First, this technique cannot distinguish whether the field is in the positive direction or negative direction. By applying an external magnetic field whose magnitude is bigger than the magnitude of a field coming from the magnetic sample, polarity of total field is fixed and actual fringing field values from the magnetic structure can be found by subtracting the external field value. Second, this technique is based on measuring shifts of resonance frequency and requires fitting to Lorentzian functions. Thus it is important to break the symmetry of the four crystal axes with respect to the direction of the external field. The values of the magnetic field used in this experiment are chosen to separate all eight ODMR lines enough to make
Figure 5.11: Micromagnetic simulation of magnetization configuration and fringing fields of a magnetic zigzag wire. Arrows inside the zigzag wire show magnetization configurations that cost lowest energy. Arrows outside of wire are fringing fields calculated by summing dipole fields of each magnetization vectors inside the zigzag wire. Calculations are done for four different probe-sample separation in $z$ direction: 0$\mu$m, 1.1$\mu$m, 2.2$\mu$m and 3.3$\mu$m. Amplitude of arrows indicates magnitude of fringing fields and colors denote magnitude of $B_z$. 

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Figure 5.12: Measurement geometry for imaging of fringing fields from zigzag wires. Blue lines are drawn along the edge of the diamond to assist measurement of angle between \( \hat{x} \) and [100] of the diamond crystal. Angle between [100] of the diamond and \( \hat{x} \) is 59°.

easy fits to eight Lorentzian functions. An ODMR spectrum taken far from the zigzag wires is shown in Fig5.13. This only measures the external magnetic field and the measured field component values extracted from the ODMR spectrum are \( B_{[100]}^{\text{ext}} = 31.96 \text{G} \), \( B_{[010]}^{\text{ext}} = -17.99 \text{G} \) and \( B_{[001]}^{\text{ext}} = 43.71 \text{G} \) using Eq.4.37. This agrees very well with values found by a gaussmeter. As the pump beam is scanned around a vertex of a zigzag wire under the external field, ODMR spectra were collected by sweeping microwave frequency. Since there are three unknown parameters, we only need three resonance lines to extract \( B_x \), \( B_y \) and \( B_z \) although having more resonance lines means better accuracy. By compromising between data acquisition time and better accuracy, we scanned the frequency to measure only the transition \( |m_s = 0\rangle \leftrightarrow |m_s = 1\rangle \) to get four resonance lines. Total magnetic field was found by fitting using MATLAB (Mathworks). By minimizing error between predicted
Figure 5.13: ODMR spectrum taken far from zigzag wires. This measures an external magnetic field only. (a) shows four crystal axes of NV centers with respect to the geometry of a bulk diamond (magenta rectangle above the crystal structure) and (b) shows ODMR spectrum taken far from zigzag wires. Eight resonance lines are due to four crystal axes as shown in (a) and two transitions: \(|m_s = 0\rangle \leftrightarrow |m_s = 1\rangle\) and \(|m_s = 0\rangle \leftrightarrow |m_s = -1\rangle\)
Figure 5.14: Vector imaging of fringing fields from a zigzag wire. (a) Scan on $xy$ plane. Scanning range is $5.5\mu m \times 5.5\mu m$. Arrows show directions and magnitudes of fields in $xy$ plane. Colors indicate magnitudes of $B_z$. (b) Scan on $zx$ plane. Scanning range is $4.4\mu m \times 4.4\mu m$. Zigzag wire is shown in perspective view. $zx$ plane was scanned at $y = 2.2\mu m$. Arrows show directions and magnitudes of $zx$ components of magnetic fields and colors indicate magnitudes of $B_z$ only.

Magnetic field values and calculated magnetic field values from resonance frequency values using Eq.4.37 for each quantization axis, the unique solution was found. The external field measured far from the zigzag wire was subtracted from the total field measured near the zigzag wire to get the local field values only. Vector field map on $xy$ plane and $zx$ plane are shown in Fig.5.14. Arrows represent direction and magnitude of $xy$ and $zx$ components of the local fields for $xy$ and $zx$ field map, respectively, and colors represent magnitude of $B_z$ components. Fig.5.15 shows line scans of $B_x$ and $B_z$ components along $x$ direction at $y = 2.2\mu m$. A magnetic field is reasonably detectable even $15\mu m$ away from the zigzag wire with magnitude of $0.01G$. One thing to note is that $B_z$ values as a function of $x$ does not show dependence of $1/r^3$. This is due to the large field gradient near the zigzag wire. Due to the fact that ensemble NV centers are measured at the surface of the diamond within the confocal...
volume, which is about 400nm × 400nm × 500nm, the variation of the magnetic field across the confocal volume broadens the resonance linewidth of the ODMR spectra. This is shown in Fig.5.16. The spectrum taken at \((x,y) = (1.1\mu m, 2.2\mu m)\) (red) shows substantial linewidth broadening compared to the spectrum taken with uniform external field only (gray). Additionally, the linewidth broadening is asymmetric due to the nature of the field gradient. This makes it very difficult to fit to a single Lorentzian function properly. For this particular spectrum, only three peaks corresponding to NV1, NV2 and NV4 in Fig.5.13 are used to extract magnetic field values. Large field gradient also means that there is a large magnetic force exerted on a magnetic particle to trap it to the vertex of the zigzag wire as shown in Fig.5.9. The magnetic force is given by

\[
F = m \cdot \nabla B
\] (5.8)

Unfortunately, it is not trivial to find the field gradient from the ODMR spectrum.

Fig.5.17 shows that there are large magnetic field gradient even far away from
Figure 5.16: ODMR linewidth broadening due to large magnetic field gradient. Red spectrum in the left side is raw data of arrow at \((x, y) = (1.1\,\mu m, 2.2\,\mu m)\) (white circle in the vector field map on the right side) and gray spectrum is ODMR with an external field only which was taken far from the zigzag wire. Dark gray solid line is fit of ODMR with the external field only to four Lorentzian functions. Substantial linewidth broadening is observed on the resonance line corresponding to NV3 (NV center index is the same as Fig.5.13)

the zigzag wire. The spectrum was measured at \((x, z) = (2.2\,\mu m, 2.2\,\mu m)\), which is indicated by a green dot, and it still shows significant linewidth broadening.

5.3.5 Conclusion

We have successfully demonstrated that three dimensional scanning vector field imaging is possible by using NV center enriched bulk diamond. We have observed the large field gradient near the vertex of the zigzag wire and this explains why magnetic particles can be trapped and manipulated. One possible solution to the linewidth broadening due to large magnetic field gradient compared to the given confocal volume of the microscope is to increase spatial resolution either by REversible Saturable Optical Fluorescence Transitions (RESOLFT) technique[11] or by using NV centers in nanodiamond. Spatial resolution using NV centers in nanodiamond is set by the
Figure 5.17: ODMR linewidth broadening due to magnetic field gradient away from the zigzag wire. Spectrum shown on the right side is measured at the green dot (closed circle) on the left side of the diagram, which is $2.2\mu m$ in $x$ and $2.2\mu m$ in $z$ away from the vertex of the zigzag wire. The spectrum reveals that there is the substantial field gradient even at a couple of microns away from the vertex of the wire.

effective diameter of NV centers which is about the same or smaller than the size of the nanodiamond. We discuss applications of magnetometry using nanodiamond in Chapter 6.
Recently, researchers have made progress in understanding of biology at the cellular level down to molecular level through the use of biolabels. Fluorophores are used as biolabels in various experiments, including direct imaging of the cells and bio-molecules, cell tracking and fluorescence resonance emission transfer (FRET), etc. However, the usefulness of commonly used fluorophores is limited due to photo-bleaching and blinking. Quantum dots are another type of the biolabels that are commonly used, but these must be encapsulated because they are toxic and will harm the biological system.

Due to its biocompatibility (non-toxicity) and photostability (no photo-bleaching and no blinking), diamond is one of the most promising candidates for a new generation of biomarkers. Additionally, there are various sizes of diamond available, from bulk crystal (on the order of millimeters in size) down to nanocrystals that are only a few nanometers in diameter. Detonation nanodiamond, for instance, has a size of 5nm or below. Combined with the unique spin properties of NV centers discussed in Chapter 4, NV center-containing nanodiamond can be used for several important applications in biology.

In this chapter, I discuss preparation of NV center-containing nanodiamond.
Then, I focus on two possible applications in biology using NV center-containing nanodiamonds. One is applications of using the nanodiamond for studies of DNA dynamics. The other is scanning vector field magnetometry for nanoscale magnetism in biology.

6.1 Creation of NV centers in nanodiamond

In order to use nanodiamond in various biological experiments, we need various sizes of the diamond nanocrystals. Thus, we purchased nanodiamond (SYP 0.09, Van Moppes) which has variations in size from 10nm and 200nm. The nanodiamond has concentration of nitrogen impurities of about 100ppm and we used electron irradiation and subsequent annealing process to create NV centers as we discussed in Sec.5.1.1. Surface defects are known to work as electron acceptors and it is not trivial to predict negatively charged NV centers (NV\(^{-}\)) production rate based on the study we did on the bulk diamonds. Thus, we used 1.5MeV electrons with a dose of \(1.04 \times 10^{19}\)cm\(^2\) to create as many NV centers as possible in each diamond nanocrystal. During the irradiation and the annealing process, surface tends to oxidize and this creates graphitic surface. It is important to remove the graphitic layers and other unknown contaminants to increase the density of negatively charged NV centers as well as to break up agglomerates. After electron irradiation and subsequent annealing, the nanodiamond was cleaned using mixture of acids. We placed the nanodiamond powder in sulfuric acid, sodium hydroxide and hydrochloric acid and boiled the solution at 90°C under reflux for a week[53]. In order to verify surface cleanliness of the diamond nanocrystals, Raman spectroscopy (FT-IR/Raman system, Renishaw) was used. The nanodiamond was dispersed on a glass substrate and excited with 457nm light. Raman spectroscopy revealed that most of the graphites was removed as shown in Fig.6.1. \(sp^2\) peaks that are clearly seen in the unclean diamond nanocryst-
Figure 6.1: Raman spectra of unclean and clean nanodiamond. The G band and the D band, which are associated with sp$^2$ bondings, are significantly suppressed after cleaning with acid under reflux. Pictures on the left side shows colors of nanodiamond solution before (blue) and after (red) cleaning process. The dark gray solution turns white after the cleaning process. The Raman data was taken by K. Wickey.

tals are significantly suppressed after the cleaning process. After the cleaning of the nanodiamonds in boiling acid under reflux, transmission electron microscopy (TEM) was used to see the surface quality and the size variations. Fig.6.2(a) shows that there are various sizes exist in the range of 10nm to 200nm. Fig.6.2(b) is a high resolution image of one nanocrystal and it shows the lattice structure of a diamond nanocrystal. However, it also shows graphitic phase of the shell and this indicates that the graphite is not completely removed after the acid cleaning under reflux and this may possibly create neutral NV centers near the surface. In order to obtain an optical spectrum and ODMR spectrum, we prepare the sample as follows. First, etched circular patterns are created on a glass coverslip (D263M, Fisher-Scientific) using a focused-ion beam (FIB) (Helius Nanolab 600, FEI). Then the glass coverslip is cleaned in Piranha solution ($\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 = 1 : 1$) for 30 minutes to remove all
the possible fluorescent contaminants that could act as background noise for our PL measurement. After nanodiamond is dispersed on the glass coverslip, scanning electron microscopy (SEM) images are taken to map out positions of each nanodiamond particle. Since the nanodiamonds are on the glass substrate, which is an insulator, we used a low energy imaging technique to avoid significant charging. The sample was brought to 2mm away from the pole piece of the SEM and a landing voltage of 1000V was used. Although the resolution of the images were not as good as images taken with high energy electrons, it was sufficient enough to measure the size and to map out positions of the nanocrystals. After a nanodiamond deposited glass piece is glued on our CPW, an optical spectrum and ODMR spectrum are taken. Fig.6.3 shows SEM and widefield fluorescence images of a nanodiamond particle and its optical spectrum. The SEM image shows that the size of the particle is about 120nm in diameter. The widefield fluorescence image (inset of Fig.6.3(a)) was taken by focusing 532nm laser beam to back aperture of the objective lens to collimate the
Figure 6.3: SEM image, widefield fluorescence image and optical spectrum of single nanodiamond. (a) SEM and widefield fluorescence images of a single nanodiamond particle. Size of the nanodiamond is about 120nm. (b) Optical spectrum of the nanodiamond shown in (a). It reveals that neutral and negatively charged NV centers coexist.

Pump beam on the sample. The FIB patterns guide us to find exactly the same spot of which we took the SEM image. Fig.6.3(b) shows optical spectrum of the nanodiamond and spectral peaks associated with both neutral and negatively charged NV centers appears in the spectrum. This is somewhat consistent with the observation from TEM images. Since negatively charged NV centers dominate the spectrum, we will not worry about the neutral NV centers here.

Because an ODMR spectrum is obtained by sweeping microwave frequency, it often requires long data acquisition time especially when there are not enough photons emitted. In order to avoid the time drift issue, we have implemented position feedback using the CCD, which is used for widefield imaging. From fitting the continuous fluorescence imaging of NV center containing nanodiamond to a Gaussian function,
we determine the peak position in $x$, $y$ and amplitude. $(x,y)$ position is used for $xy$ position feedback and amplitude is used for $z$ position feedback. Fig.6.4 shows ODMR spectra taken from two single diamond nanocrystals (NVND2 and NVND3) under an external magnetic field of 72G. Size of the nanodiamond (NVND3) measured by a SEM image is about 200nm. The ODMR spectrum of NVND3 shows clear eight resonance line splittings and this also confirms that we measured ensemble NV centers in a single nanodiamond particle. The ODMR spectrum of NVND2 shows different spectral behavior and this is due to the orientation of crystal, which is different from the orientation of NVND3. Having developed the technique to measure an ODMR from a single nanodiamond combined with vector field imaging (as we discussed in Chapter 5), we now apply our technique to two different biological systems: first, studying DNA and chromatin dynamics and second, obtaining vector field imaging of nano-magnetism in biological systems.

6.2 Study of dynamics of DNA using NV center magnetometry

6.2.1 Motivation

The human genome is highly complex and possesses outstanding functionality and organization on multiple length scales (Fig.6.5(a)). The dynamics of chromatin fibers, which are composed of DNA molecules wrapped about histone octamers, are almost completely unexplored. There has been only one paper\cite{98} published on a quantitative study of the dynamics of chromatin. It is known that properties of chromatin regulate gene expression\cite{99} and cell division\cite{100}. Thus, study of genome material properties will allow us to understand genome expression, replication and repair. This requires the study of genomic materials \textit{in vivo} but there are no techniques available to study such system. Here we propose a new technique that measures dynamics of the genomic
Figure 6.4: ODMR spectra of single nanodiamond particles. The ODMR spectra shown on the right are taken from single nanodiamond particles (NVND2 and NVND3) shown on the left side. Optical widefield image was taken by exciting all the nanodiamonds within the field of view with a collimated 532nm laser beam. The SEM image of NVND3 indicates that NVND3 is possibly a single particle. Low resolution of the image is due to the low energy of e-beam to minimize a charging effect since the substrate is a glass coverslip, which is insulating. The ODMR spectrum shows clear eight resonance line splittings confirming that this is a measurement of ensemble NV centers in a single nanodiamond particle. Due to the randomness of orientations of diamond nanocrystals, NVND2 and NVND3 shows different spectra in the same external magnetic field.
materials *in vivo* using NV centers in a nanodiamond. The ODMR magnetometer that we developed in Chapter 5 provides us with the means to probe the dynamics of genomic materials such as a single DNA molecule to higher order chromatin fibers.

In order to develop this technique we start with studying dynamics of DNA since it is relatively well known material. For the DNA measurements, we use ODMR of NV centers in nanodiamond to measure the rotation, tilting, and length fluctuations of attached DNA molecules which have been selectively labeled with the nanodiamond or biogenic magnetic nanoparticles. Fig.6.5(b) shows simple schematics of how we will measure the dynamics of a DNA molecule/chromatin fiber. A nanodiamond label is selectively attached to a specific histon or a DNA molecule and the fluctuation of the DNA are reflected in the ODMR spectrum under a given external field. More detailed experimental design is discussed in the next section.

### 6.2.2 Two measurement schemes

We can measure dynamics of DNA in two different ways. The first, I will refer to as the *diamond scheme* and the other as the *magnetic bead scheme*. This is schematically shown in Fig.6.6. In the *diamond scheme*, we can prepare a sample, in which one end of DNA is bound to a surface and a nanodiamond particle is attached to the free end of the DNA strand. Measurements can be taken under a static uniform external magnetic field and the position of the nanodiamond in $\hat{z}$ direction does not affect the ODMR spectrum. However, as the nanocrystal undergoes rotational fluctuation by the random fluctuation of the DNA, NV centers in the nanodiamond experience different external fields due to the orientation of the NV crystal axes. Depending on the range of the rotational motion, the spectral linewidth broadening is different. By studying the ODMR spectrum, we should be able to extract information of the rotational fluctuations. Fig.6.7 shows simulations of two different situations.
Figure 6.5: Multiple length scale of genomic material and measurement scheme of DNA dynamics. (a) Multiple length scale of genomic materials. Our focus is on nucleosomes and chromatin fibers. (b) Simple schematic diagram of an experimental design. A nanodiamond will be attached to a specific histon or a DNA molecule. Fluctuation of the chromatin fiber will be reflected on ODMR spectrum under an external magnetic field.
Figure 6.6: Two measurement schemes to measure DNA dynamics using NV centers in nanodiamond.

Both (a) and (b) are the case when the external field of 108G is applied to a single nanodiamond which is attached to a free end of the DNA while the other end of the DNA is bound to the surface. Initial orientation of nanodiamond, when DNA is static, is completely random. Orientation of the nanodiamond is fluctuating with normal distribution due the Brownian fluctuation of the DNA. Here we set standard deviation of the normal distribution to be 15° in each rotation axis. The DNA can be controlled to be either randomly fluctuating within a range determined by its mechanical properties or rigidly fixed. Rigidity of DNA can be controlled both by flow of solution past the DNA strands, as well as concentration of Mg²⁺ ions in the solution. Fig.6.7(a) shows the situation when the nanodiamond is oriented in a certain way that eight resonance lines are well separated in the case of a fixed DNA molecule. This corresponds to the measured ODMR of NVND3 shown in Fig.6.4. When the DNA
is randomly fluctuating with the sigma distribution of 15°, each resonance line for the static situation is not separated far enough and the whole spectrum is broadened when the DNA is fluctuating. In this case, little useful information can be extracted from the data. Fig.6.7(b) is the situation when direction of the nanodiamond is such that two crystal axes with respect to an external magnetic field are degenerate (or slightly separated). This corresponds to the measured ODMR of NVND2 shown in Fig.6.4. In this type of situation, we should see significant and obvious broadening of our resonance peaks with increased motion of the DNA (on the order of 100MHz linewidths), which typically have a linewidth of 10MHz or less under static conditions. This broadening linewidth can be measured as function of DNA fluctuations, which will be controlled using the flow of solution past the DNA (increased flow will reduce the Brownian motion of the DNA) as well as the concentrations of Mg$^{2+}$ ions in solution, which will affect the stiffness of the DNA. These two case studies reveal that control of the orientation of diamond nanocrystal is important for obtaining meaningful spectral features to measure motional fluctuations.

The second experimental scheme is attaching the diamond nanocrystals to the glass substrate so that they are fixed in position and orientation, then attaching the DNA strands directly onto the diamond nanocrystals, followed by attaching a magnetic bead to the free end of the DNA strand. I will refer to this as the magnetic bead scheme. Fluctuations in the DNA configuration, which can be controlled by flow of solution, an externally applied magnetic field gradient, or concentration of the Mg$^{2+}$ ions in solution, can be quantitatively evaluated through the magnetic field of the bead, which causes broadening and shifting of the resonance lines in the ODMR spectra collected from the diamond. In this scheme, ODMR spectrum is not sensitive to rotational fluctuations. However, this is very sensitive measurement scheme to measure fluctuations of end-to-end distance of the DNA since the NV centers in the
Figure 6.7: Simulations for diamond scheme. (a) and (b) shows ODMR spectra in an applied external field when DNA is fixed (blue) and when DNA is randomly fluctuating (red) with the standard deviation of the normal distribution to be 15°. (a) is the situation when the nanodiamond is oriented in a certain way that eight resonance lines are well separated in the case of a fixed DNA molecule. This corresponds to the measured ODMR of NVND3 shown in Fig.6.4. (b) is the situation when direction of the nanodiamond is such that two crystal axes with respect to an external magnetic field are degenerate (or slightly separated). This corresponds to the measured ODMR of NVND2 shown in Fig.6.4. Both cases are calculated in the same external field (108G) but in different crystal orientations. These two case studies reveal that the orientation of the nanodiamond is important for obtaining meaningful spectral features to understand motional fluctuations.
diamond nanocrystal probes magnetic field from the magnetic nanoparticle.

In order to estimate scaling of diamond crystal size, magnetic bead size and bead spacing, we can do the following analysis. The magnetic field of a bead is given by

$$B_z = \frac{8\pi M_s}{3} \left( \frac{a}{z} \right)^3 \quad (6.1)$$

where we assume that $4\pi M_s \simeq 5kG$ is the saturation magnetization of the magnetic bead, $a$ is its radius and $z$ is the distance from the center of the bead to the center of the nanodiamond. The upper limit of the field from the particle is set by the requirement that the field spread $\Delta B_z$ across the diamond be significantly less than $B_z$, say $\Delta B_z \simeq B_z/\alpha$. $\Delta B_z$ depends on the diameter of the diamond nanocrystal, $d_d$

$$\Delta B_z = \frac{\partial B_z}{\partial z} d_d \quad (6.2a)$$

$$= -3B_z \frac{d_d}{3\alpha} \quad (6.2b)$$

$$d_d = \frac{z_{DNA}}{3\alpha} \quad (6.2c)$$

where $z_{DNA}$ is the distance from the center of the bead to the center of the diamond set by the end-to-end distance of the DNA. $z_{DNA}$ is defined by $z_{DNA} = \sqrt{bL}$ where $b = 50\text{nm}$ is the DNA persistence length and $L$ is the DNA contour length. For $\alpha = 3.3$ and $z_{DNA} = 1\mu\text{m}$, $d_d \sim 0.1\mu\text{m}$.

The minimum field $B_{\text{min}}$ we wish the bead to apply to the diamond will determine its minimum radius $a_{\text{min}}$

$$B_{\text{min}} = \frac{8\pi M_s}{3} \left( \frac{a_{\text{min}}}{z_{DNA}} \right)^3 \quad (6.3a)$$

$$\frac{a_{\text{min}}}{z_{DNA}} = \left( \frac{3B_{\text{min}}}{8\pi M} \right)^{1/3} \simeq 0.07B_{\text{min}}^{1/3} \quad (6.3b)$$

Setting $B_{\text{min}} \sim 10G$, which is constrained by the linewidth of the spectrum, and $z_{DNA} = 1\mu\text{m}$ gives $a_{\text{min}} \sim 150\text{nm}$. From Eq.6.1 and Eq.6.3b, we can estimate a
distance between the nearest neighbor beads, \( l_{\text{nn}} \), to be \( l_{\text{nn}} = \beta^{1/3} z_{\text{DNA}} \). For \( \beta \) in the range of 10 to 100, \( l_{\text{nn}} \) will be in the range of 2 to 5\( \mu \text{m} \).

Using these numbers as a guideline, we can also run numerical simulations to predict what spectral features we expect due to the DNA fluctuations. For the numerical simulations, we used the radius of the nanodiamond to be 100nm (This is the biggest size of the diamond nanocrystal we have and this will generate brightest PL for most of the cases), radius of magnetic bead to be 250nm (Functionalized ferromagnetic beads are commercially available with size down to 250nm in radius). We set the contour length of DNA (\( L \)) to be 16\( \mu \text{m} \), which is the standard length of \( \lambda \)-DNA we will use (prepared in Prof. Poirier’s lab). The diameter of the Brownian motion of the DNA is set to be the same as average end-to-end distance of the DNA, which is \( \sqrt{6}L \). Fig.6.8 shows the result of the numerical simulation of ODMR for transitions between \( |m_s = 0\rangle \leftrightarrow |m_s = 1\rangle \). The black curve is the ODMR spectrum only with an applied external magnetic field (without the magnetic bead). The blue curve is the ODMR spectrum when the magnetic bead is attached to a free end of the DNA with \( L = 16\mu \text{m} \) under the applied external field. This is the case when DNA does not experience any external force and undergoes random fluctuation. The average magnetic field value from the magnetic bead experienced by the nanodiamond is about 9G in this case. The red curve is the ODMR spectrum when the magnetic bead is attached to a free end of the DNA with \( L = 8\mu \text{m} \) under the applied external field. This is the situation when the length of DNA is shortened because the molecule is binding to proteins with which the DNA is labeled. The average magnetic field value from the magnetic bead experienced by the diamond nanocrystal in this case is about 21G. However, this discussion is very much depending on the value of the remanent magnetization of the magnetic bead, which is not very different from the saturation magnetization for the single crystalline bulk ferromagnetic materials if they are
Figure 6.8: Numerical simulations for magnetic bead scheme. The black curve is the ODMR spectrum with an applied external field only (without the magnetic bead). The blue curve is the ODMR spectrum when the magnetic bead is attached to a free end of the DNA with $L = 16\mu m$ under the same external magnetic field. The average magnetic field from the magnetic bead experienced by the diamond nanocrystal is about 9G. The red curve is the ODMR spectrum when the magnetic bead is attached to a free end of the DNA with $L = 8\mu m$ under the same external magnetic field. In this case, the average magnetic field from the magnetic bead experienced by the diamond nanocrystal is about 21G.
aligned into the easy axis with respect to an external magnetic field. It turns out that this is not trivial for magnetic nanoparticles and this leads us to characterize the magnetic properties of the magnetic bead.

6.2.3 Magnetic nanoparticle characterization

The magnetic beads (SiMAG, Chemicell) we use here are all commercially available and functionalized. They are composed of a magnetite ($\text{Fe}_3\text{O}_4$) core in a silica matrix. The magnetic beads we use are ferromagnetic and have Amine groups\textsuperscript{6}, coating the surface. They are available in the size of 500nm, 750nm and 1$\mu$m in diameter and we characterized for two different sizes, 500nm and 750nm, for our experiment. Fig.6.9 shows a scanning transmission electron microscopy (STEM) image of the 500nm Chemicell bead and its energy dispersive X-ray (EDX) spectrum. The core is composed of several small particles in the range of 100 to 200nm and a silica matrix is not visible in the STEM image. The EDX spectrum reveals that material is iron-oxide. A silicon peak from the silica matrix also appears even though it is not visible in the STEM image. Copper and carbon peaks are from the grid that holds the Chemicell bead for STEM measurement. Because the core is not purely a single particle, it is not trivial to know how it behaves magnetically.

Additionally, we performed a superconducting quantum interference device (SQUID) magnetometry measurement of these particles. Fig.6.10 shows SQUID data on two different sizes of magnetic beads, 500nm and 750nm in diameter. From the density of the each size of the beads, the saturation magnetization of each was found out to be $0.5 \times 10^{-14}\text{J/T}$ for the size of 500nm and $1.45 \times 10^{-14}\text{J/T}$ for the size of 750nm. However, the remanent magnetization is found to be about ten times less than the saturation magnetization for each size. This may not reflect magnetic properties of

\textsuperscript{6} Bead $- \text{Si-}(\text{CH}_2)_3-\text{NH}_2$
Figure 6.9: A STEM images and an EDX spectrum of a Chemicell magnetic particle. The STEM image reveals that the core is not a single particle but consists of multiple particles embedded in a silica matrix. The EDX spectrum shows that the material is iron-oxide and has a silica shell although the silica shell is not visible in the STEM image. The red box in the STEM image indicates the area where the EDX spectrum was collected.

individual particle because this is an ensemble measurement. Thus, magnetic moment of an individual magnetic particle needs to be measured as a function of an external magnetic field to find out right parameters to properly design an experiment using magnetic bead scheme. Magnetic characterization of a single magnetic particle could be done by more sophisticated method such as the cantilever magnetometry[101] measurement and is highly desirable in the future.
Figure 6.10: SQUID magnetometry measurement of the Chemicell magnetic beads. Saturation magnetization of an each particle with the size of 500nm in diameter is measured to be $0.5 \times 10^{-14}$ J/T. Saturation magnetization of an each particle with the size of 750nm is $1.45 \times 10^{-14}$ J/T. Remanent magnetization is found to be more than 10 times smaller from the SQUID magnetometry measurement.
6.3 Toward magnetic field imaging of magnetotactic bacteria

6.3.1 Motivation

NV center magnetometry using diamond nanocrystal can also be applied to study nanoscale magnetism in vivo. For instance, abnormal accumulation of iron and dysregulation of iron transport and storage in human brain tissue has long been associated with Alzheimer’s disease, Huntington’s disease, and Parkinson’s disease[102]. These high iron concentrations are due to accumulations of biogenic magnetite. These can serve as a biomarker for early diagnosis of the diseases. Understanding magnetic properties of nanometer-sized magnetite in cellular environments can provide foundation for imaging biogenic iron in more complex biological systems such as human brain tissue.

Here, I propose to use NV center magnetometry using nanodiamond to study the properties of the magnetotactic bacteria such as Magnetospirillum Gryphiswaldense (MSR1). These magnetotactic bacteria internally mineralize long, uniform chains of biogenic, magnetite nanoparticles. These are quite similar biological systems to the human brain tissues with high magnetite concentrations since both systems have magnetite particles mineralized with 10s of nanometers in size. The magnetotactic bacteria is easy to grown in the lab and thus is a suitable system to develop scanning NV center magnetometry for biological tissues.

6.3.2 Growth of MSR1

Magnetospirillum Gryphiswaldense (MSR1) (6361, DSMZ) strain was purchased and R. Teeling grew it further in collaboration with Prof. Poirier’s group. The growth solution was made by mixing 2.38g of 4-(2-hydroxyethyl)-1-piperazineethanesulfonic...
acid (Hepes), 3g of Sodium Pyruvate, 0.1g of Yeast Extract, 3g of Soybean Peptone, 0.34g of Sodium Nitrate, 0.1g of Potassium Phosphate Monobasic, 0.15g of Magnesium Sulfate Heptahydrate and DI water to make total volume of 1L\[103]. Then pH was adjusted to 6.97 by adding Sodium Hydroxide. After autoclaving growth tubes, flasks, etc, 1mL of Ferric Quinate was mixed with 0.5mL DL-Dithiothreitol (DTT) to give 20µM iron concentration and 1mM DTT concentration. All the growth tubes had 15mL of growth medium added with 1.5mL DTT and Ferric Quinate mixture.

Cultivation was carried out under aerobic and microaerobic conditions. For aerobic cultivation, cells were incubated in free gas exchange condition with air only by covering the growth tubes with plastic cabs. For microaerobic cultivation, the growth tubes were heated over a flame and then capped with rubber stopper. All the growth tubes were left for ten days. The best magnetite chains were formed in the microaerobic condition. After the growth of the MSR1 strain, SEM, AFM and MFM imaging were performed and these are shown in Fig.6.11. STEM imaging shows a structure of biogenic magnetite nanoparticle chains with high resolution (Fig.6.12). The sizes of

Figure 6.11: SEM, AFM and MFM images of MSR1. All the images are taken from the same MSR1. MSR1 was magnetized out of plane for MFM imaging. A MFM image shows clear magnetic contrast. Scan size of all the images is 3µm × 3µm.
the magnetic particles are in the range of 30nm to 55nm and the separations of the particles are in the range of a few to 10nm. The STEM image of the magnetite chain used for numerical simulations to predict the stray field, which will be mapped using our NV center magnetometry technique. This will be discussed in Sec.6.3.4.

6.3.3 Magnetic characterization of MSR1

The magnetic properties of these bacteria were characterized by SQUID magnetometry. The M-H curve in Fig.6.13(a) shows typical ferromagnetic behavior of magnetotactic bacteria. Inset of the Fig.6.13(a) shows a test with a magnet. A rare-earth magnet at the surface of the growth tube attracts all the bacteria that have a magnetite chain inside and form a spot with high contrast. Fig.6.13(b) shows remanent magnetization measurement at zero field and clearly shows Verwey transition at 100K, which is a typical characteristic of stoichiometric nanoparticulate magnetite[104]. The Ver-
Figure 6.13: SQUID magnetometry measurement of MSR1. (a) A M-H curve of MSR1 shows typical ferromagnetic behavior of the MSR1. The coercive field is measured to be 130G. Inset shows simple magnet test. A rare-earth magnet was held at the surface of the growth tube and all the bacteria that have a magnetite chain inside are attracted by a magnetic force and form a spot. (b) Remanent magnetization as a function of temperature. The data clearly shows Verwey transition at 100K and this is one of the clear evidence of stoichiometric nanoparticulate magnetite[104].

The Verwey transition is the stoichiometric change of magnetite from a inverse spinel structure \( ([\text{Fe}^{3+}]_A [\text{Fe}^{3+}\text{Fe}^{2+}]_B \text{O}_4) \) above \( T_v \) (Verwey temperature) to a normal spinel structure \( ([\text{Fe}^{2+}]_A [\text{Fe}^{3+}\text{Fe}^{3+}]_B \text{O}_4) \) below \( T_v \). Typical Verwey transition of bulk magnetite is at 122K but the transition is observed at 100K for magnetite nano-particles[104].

### 6.3.4 Vector field simulation of magnetotactic bacteria

Stray fields from the MSR1 were simulated in the same way discussed in Sec.5.3.3. OOMMF parameters used in this simulation are as follows[105]: \( M_s = 3.98 \times 10^5 \text{A/m} \), \( K_1 = 27 \times 10^4 \text{J/m}^3 \), \( A = 1.2 \times 10^{-11} \text{J/m} \), cubic anisotropy is along \([111]\) and \([100]\), damping constant = 0.005, the thickness of individual particle = 53nm and the cell size = 3.23nm. The size of the NV center containing diamond nanoparticle is 15nm and the field values are averaged over the volume corresponding to the size of the
Fig. 6.14 shows stray field measured by a NV center probe at two different sample-probe distances. Fig. 6.14(a) shows a vector field map for the 25nm of a sample-probe distance. Vector field maps of $xy$ and $z$ components of the stray magnetic fields are shown by black arrows (on the right side) and colors (on the left side), respectively. White arrows inside the magnetite particles on the left side show $x$ and $y$ components of magnetic moments of the particle and red (blue) denotes positive (negative) values of $z$ components of magnetic moments. The maximum field values of each component are \{165.86, -169.17, -281.15\} in gauss. These are high field values and individual particles are resolvable as clearly seen in the $B_z$ components field map on the right side. The individual particles are resolvable even at 50nm of a sample-probe distance (not shown here). Fig. 6.14(b) shows a vector field map for the 150nm sample-probe distances. The maximum field component values are \{7.56, -11.77, -16.7\} in gauss. These field values are still large enough to measure with NV center magnetometry but the right side of the figure shows that individual particles are no longer resolvable. This simulation results show that this measurement is all possible at room temperature with the field sensitivity of our setup.

6.3.5 Proposed setup of scanning N-V center vector magnetometry for magnetic imaging of magnetotactic bacteria

Now I propose experimental geometry as shown in Fig. 6.15. Diamond nanocrystals are dispersed on the coplanar waveguide. Individual nanodiamonds have multiple NV centers with more than three NV crystal axes. This enables us to do vector field imaging without changing the orientation of the external magnetic field. In case of using nanodiamond with single NV center, at least three different orientation of the external magnetic field is required to find out the crystal orientation of the diamond to perform vector field magnetometry. Another advantage of this setup is
Figure 6.14: Simulations of stray fields from MSR1. (a) The sample-probe distance is 25nm. The right (left) side shows field components of $B_{xy}$ ($B_z$). Arrows represent direction and red (blue) indicates positive (negative). Magnetic moment configurations of magnetite chain in MSR1 are also shown on the left side. The inset shows the original STEM image of MSR1 used in this simulation. (b) The sample-probe distance is 150nm. Individual particles are no longer resolvable although magnitude of the stray field is still measurable with our NV center magnetometry.
that any diamond nanocrystal can be chosen as a probe. It is possible to choose different size, brightness, orientation, etc., by moving the coplanar waveguide. The size can be estimated and chosen with the assistance of SEM images as we have shown in the previous sections. One of the most advantageous aspects of this setup is that we have an optical access. While we approach our sample toward the diamond nanoparticle using a cantilever, motion and position of the sample can be monitored and this makes the measurement so much easier. Unlike an experiment in which the nanodiamond particle is glued at the tip of an AFM cantilever, the preparation of the probe is extremely easy and switching to another NV center probe is very simple in case of damage or loss of the diamond nanoparticle. No feedback is required for the objective lens to keep track of the diamond nanoparticle as it is true for scanning nanodiamond on a cantilever. There is no obstruction to collect photons from the NV center in comparison to nanodiamond on a cantilever geometry, which usually experiences loss of photons blocked by sample to measure. For this reason, photons are usually collected from the side. As a result, optical access is lost. Additionally, any use of glue can be avoided in this geometry.
Figure 6.15: Proposed experimental setup for scanning vector magnetometry using nanodiamond. The key aspect of this setup is to scan biological sample on a cantilever and the NV center containing diamond nanocrystals, which serves as magnetic field probe, are dispersed on a CPW.
Chapter 7
CONCLUSIONS

In this dissertation, we covered optical studies of spin systems in three different materials: gallium arsenide, europium titanate and nitrogen-vacancy centers in diamond. First, polarization of spins in GaAs was created by optical pumping and manipulated using an external magnetic field. The status of these spins was detected by measurement of spin-PL. we studied the spin relaxation time of bulk and membrane GaAs via the Hanle effect, in which spins are made to precess by perpendicular external field. Additionally, we studied spin diffusion effect on the Hanle effect by controlling pump spot size. This work laid a foundation for developing a material non-specific spin detection technique for paramagnetic materials by combining optical detection with magnetic scanned probe. Second, we studied the multiferroic properties of europium titanate on dysprosium scandate which is a new class of multiferroic material whose properties are controlled by strain engineering. Magneto optical Kerr effect (MOKE) was used to measure magnetic properties of the europium titanate under strain in a cryogenic condition. We showed that the ferromagnetism coexists with ferroelectricity and they are also coupled. Finally, we studied localized electron spins of negatively charged nitrogen-vacancy (NV) centers in diamond using optical detection and possible applications to biological systems. The spins of localized electrons of NV centers can be polarized, manipulated and detected by optically detected magnetic resonance
(ODMR) with a high resolution. Using such unique spin properties, scanning vector field magnetometry was developed using bulk diamond and vector field imaging of a magnetic trap was presented here. We also discussed two possible applications of NV center magnetometry using nanodiamond for biological systems. Dynamics of DNA was proposed to be measured using NV center magnetometry. Theoretical estimation shows that this is a sensitive and unique approach to measure dynamics of DNA and chromatin fibers with a spectroscopic precision. Scanning vector field imaging of magnetotactic bacteria was also proposed here. Numerical simulations show that this is feasible and can possibly be used to study imaging of nanomagnetism \textit{in vivo} in biology.
Bibliography


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