Sensitive Magnetometry Based on NV Centers in Diamonds

Author:
Amir Waxman

A thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Physics Department

Submitted to the Senate of Ben-Gurion University of the Negev

January 15th, 2014

Beer-Sheva
This work was carried out under the supervision of Professor Ron Folman

In the Physics department

Faculty of Natural science
Declaration of Authorship

I Amir Waxman, whose signature appears below, hereby declare that:

■ I have written this Thesis by myself, except for the help and guidance offered by my Thesis Advisor.

■ The scientific materials included in this Thesis are products of my own research, culled from the period during which I was a research student.

■ This Thesis incorporates research materials produced in cooperation with others, excluding the technical help commonly received during experimental work. Therefore, I am attaching another affidavit stating the contributions made by myself and the other participants in this research, which has been approved by them and submitted with their approval.

Signed: Amir Waxman

Date: 15.1.14
Abstract

Physics department

Doctor of Philosophy

Sensitive magnetometry based on NV centers in diamonds

by Amir Waxman

In recent years the nitrogen-vacancy (NV) center in diamond has emerged as an atom-like system with many applications in precision measurements, quantum information processing and quantum fundamental research. In this thesis we focus on magnetometry with NV centers which exhibits high sensitivity as well as high spatial resolution.

During my Ph.D studies I have dived into this subject which is completely new in our lab. I have constructed from scratch the experimental system comprising of a confocal microscopy imaging setup, liquid helium based cryogenic system and computerized experimental control. In addition, I have prepared and characterized diamond sensors especially designed for this work, and designed as well as fabricated integrated superconducting chips to serve as the probed samples in the magnetometry experiments.

The most popular spectroscopy method used for NV magnetometry is called optically detected magnetic resonance (ODMR). The width of the spectroscopic signal and its contrast have a direct implication
on the magnetic sensitivity enabled by the sensor. In this thesis we have explored several factors affecting the ODMR signal such as the power of the radiation sources, the detection efficiency of the optical system and the polarization of the excitation light. In a collaboration with the lab of Dmitry Budker in the University of California at Berkeley, we have investigated the effect of fluctuations in temperature on the stability of the NV magnetic sensor, and found the error to be in the order of $\sim 3 \text{nT/mK}$. At BGU we have characterized a diamond sensor prepared in our lab and found it to have $\sim 1 \mu\text{T}/\sqrt{\text{Hz}}$ sensitivity.

In order to demonstrate the significant potential the sensor has for fundamental scientific research as well as technological applications, the main project which we have been working on is the magnetic imaging of superconductors with NV centers. A deep understanding of superconductors, especially those operating at high temperatures, is still missing. Due to the properties of NV’s, such a technique has the potential to image a single vortex and perhaps even to monitor the inter-vortex dynamics. For this experiment we have implanted an extremely thin layer ($\sim 10 \text{ nm}$) of NV centers on the diamond. We have used a sensitive detection system and lock-in techniques to characterize a thin layer of a superconductor of the type Ytterbium Barium Copper Oxide (YBCO): we have found the critical temperature of the YBCO layer to be $T_c = 70.0 \pm 0.2 \text{ K}$ and determined the external magnetic field at which vortices start to form to be $H_P = 46.2 \pm 3.9 \text{ G}$. For future experiments we have fabricated a superconducting chip with which we will be able to test the ability of our method to resolve a single vortex. We also demonstrate here the simulated single vortex imaging signal proving such a measurement is indeed feasible.
Publications based on this research


Acknowledgements

This work wouldn’t be possible without the help and support of others. I am grateful to Dmitry Budker, Victor Acosta and Andrejs Jarmola from Berkeley who hosted me there twice for a total period of almost three months during which they taught me the basic foundations of NV magnetometry. Not only have I learned a lot from you guys, but you have also taken care of entertaining me after the work hours making my stay there both educational and enjoyable. The connections with the Berkeley people did not end in these visits but rather were developed into a fruitful collaboration which still exists and into a friendship I hope will survive the time difference. During the work on the paper now submitted to Physical Review B I got a lot of help from the Berkeley collaborators in rewriting and editing the paper. Louis Bouchard from UCLA has also contributed his skills to the writing of the manuscript as well as giving me useful ideas throughout my Ph.D studies. I would also like to thank Eli Zeldov from the Weizman Institute and Vladimir Kresin from Berkeley for stimulating discussions throughout the writing of the paper.

During my studies, I found the help of my colleagues in the lab very useful. Thank you guys for giving me both technical and moral support and contributing from your experience and wisdom to my work. Among my colleagues I would like to mention Menachem Givon who not only trained me as a Master’s student but also provided technical advice during the present work. I am also thankful to David Groswasser who gave his help when I was skeptical regarding the possibility my experiment would ever work. Yaniv Bar Haim had also spent much time to help me. I find it worth mentioning that Yaniv is probably the only guy around who is capable of finding a 80 µm thick half-transparent diamond in a 1 by 1 meter space at 10:00 pm, while being distracted by a whining Ph.D student. Thank you Yaniv for that. Special thanks are also devoted to Yoni Japha and Mark Keil who helped me to edit my thesis. In addition, I thank the rest of the lab people for all kinds of support I got from them during the last five years. I gratefully acknowledge the people of the fabrication facility in Ben-Gurion University for designing and fabricating chips for me. In particular, I thank the fab worker Yacov Bernstein who enriched my knowledge both in chip fabrication and in European football. I also acknowledge Aharon Tabibian and the team of the mechanical workshop who made all the parts I have ordered rapidly and with no faults.
At the beginning of my research I was the only guy working with NV centers in our lab. Hezi Schlussel put an end to this solitude when he came to do his Ph.D with me. Thank you Hezi for helping me out in the experiment and for suffering my moods whenever nothing worked. I wish you success in your own research, and hope you have learned at least some useful things from me.

Finally, I would like to thank my advisor Ron Folman. I started working at your lab eight years ago, and during this time I have learned a lot from you. Thank you for introducing me to the great world of quantum physics, and for giving me the chance to work in this interesting and amazing field of NV centers. Thank you for insisting that I work on my documents until they are impeccable and rehearse my talks until they are fluent. Thank you for helping in difficult times and for sharing my happiness with me in better times. I am sure these things you have given me will help me in the future, both in my career and my private life.

The work in the lab is very demanding and it is hard to succeed without the support and help of the family. I would like to thank my mother and father for giving me all the love in the world and educating me for ambitiousness and perseverance. I am thankful to my wife Liat who gave me all the conditions to succeed. I am sorry for all these times that you felt you are talking to the wall while I was running some formulas in my head. And last but not least, thank you Guilad, my son. You came into my world a year ago, and since then even the worst day gets better when I come home and kiss you.
## Contents

<table>
<thead>
<tr>
<th>Declaration of Authorship</th>
<th>ii</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>iii</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>vi</td>
</tr>
<tr>
<td>Contents</td>
<td>viii</td>
</tr>
<tr>
<td>List of Figures</td>
<td>x</td>
</tr>
<tr>
<td>List of Tables</td>
<td>xii</td>
</tr>
</tbody>
</table>

### 1 Introduction
1.1 State of the art .............................................. 3
1.2 Thesis outline ............................................... 5

### 2 Physics of nitrogen vacancy centers in diamond 7
2.1 Generation of the nitrogen vacancy defect in diamond. 7
2.2 $C_{3v}$ group symmetries and the NV structure ........... 8
   2.2.1 Electronic configurations .............................. 9
   2.2.2 Electric dipole transitions ............................ 12
   2.2.3 Photoluminescence spectrum of the NV centers ....... 16
   2.2.4 Intersystem crossing and optical pumping ........... 18
2.3 ODMR spectroscopy of the NV ground state and sensitive magnetometry ............................. 19
   2.3.1 ODMR spectroscopy ..................................... 19
   2.3.2 The ground state Hamiltonian .......................... 21
### Contents

2.4 NV magnetometry ........................................... 24
   2.4.1 Ensemble NV magnetometry ....................... 27

3 Characterization and optimization of NV sensors .... 30
   3.1 Experimental technique ................................. 31
      3.1.1 Optimization of the ODMR setup ............... 35
      3.1.2 Rabi spectroscopy ................................. 39
   3.2 Temperature dependence of the ODMR signal ....... 41
      3.2.1 Background and motivation ....................... 41
      3.2.2 Calculation of $D$ ............................... 42
      3.2.3 Experimental results ............................. 43
   3.3 Polarization-selective excitation .................... 47
      3.3.1 Background and motivation ....................... 47
      3.3.2 Experimental results ............................. 49
   3.4 Summary: Properties of a magnetic sensor developed at Ben-Gurion University .................. 55

4 Diamond magnetometry of a thin film superconductor 62
   4.1 Background and motivation ............................. 62
      4.1.1 Special properties of a thin film superconductor 67
   4.2 Superconducting thin film characterization with a diamond magnetometer .................. 69
      4.2.1 Experimental technique ............................ 69
      4.2.2 Experimental results ............................. 73
   4.3 Towards on-chip vortex imaging ....................... 82
      4.3.1 Vortex imaging simulations ....................... 83
      4.3.2 Chip fabrication ................................. 85
   4.4 Conclusions and outlook ............................... 88

5 Summary ......................................................... 90

Bibliography .................................................... 92
List of Figures

1.1 A diagram comparing the various magnetic sensing methods ........................................... 5

2.1 Structure and symmetry operations for the NV system. ............................................. 10

2.2 (a) The ground state electronic configuration. According to Hund’s rule the spins in both e orbitals are aligned in the same direction. (b) One of the possible wave functions in the first excited configuration, \(|a_1 e_y\rangle \uparrow \uparrow\). ................................................................. 13

2.3 Illustration of the Franck-Condon rule via a schematic of the NV system excitation and emission. ................................................................. 17

2.4 Schematic of the NV energy states under room temperature conditions. ....................... 20

2.5 Properties of the NV ground state ......................... 25

2.6 Magnetic field orientations and the corresponding ODMR spectra for the three possible crystallographic planes. ................................................. 29

3.1 A diagram of the experimental system ......................... 31

3.2 Dependence of the ODMR linewidth on the microwave power. ................................. 36

3.3 Laser narrowing of the ODMR spectral line. ................................. 37

3.4 Different optical setups for the collection efficiency testing experiment. ................................. 40

3.5 Room temperature Rabi oscillations between the \(m_s = 0\) and \(m_s = -1\) levels. ................................. 41

3.6 Zero-field ODMR. ................................................................. 44

3.7 The variation of \(D\) with temperature. ................................................................. 45

3.8 \(D\) vs. \(T\) over a wide range of temperatures. ................................................................. 46

3.9 Theory of polarized excitation. ................................................................. 49

3.10 The effect of polarization angle on the ODMR spectrum. ................................................................. 51
3.11  Lock-in technique for selective polarization excitation. 52
3.12  Experimental measurements of the contrast for resonances representing the various NV orientations vs. the green light polarization for a \{100\} diamond. 53
3.13  An illustration of the fluorescence anisotropy for NV centers. 55
3.14  An ODMR spectrum of the Sumi diamond. 57
3.15  Lock-in ODMR spectra. 59

4.1  An illustration of the two characteristic lengths of a superconducting vortex. 63
4.2  An illustration of the effect of geometry on the external field lines and vortex penetration. 69
4.3  The experimental setup. 72
4.4  Signal enhancement of the diamond sensor. 74
4.5  Detection of the superconducting phase transition using ODMR spectroscopy. 77
4.6  The vortex penetration field detection. 80
4.7  Two different configurations for optical imaging. 83
4.8  Simulation of the single vortex magnetic detection. 86
4.9  Different stages in the fabrication of the superconductor chip. 87
List of Tables

2.1 A character table for the $C_{3v}$ group elements in the different IRs. The elements indicating rotations by $0^\circ$ ($360^\circ$), $120^\circ$ and $240^\circ$ are denoted $I$, $C_3$ and $C_3^{-1}$, respectively. The elements indicating reflections are denoted $R_1$, $R_2$ and $R_3$. .................................................. 9

2.2 Wave functions and $C_{3v}$ symmetries for the electronic configurations $e^2$ and $ae$ of the NV center. The notation $S(T)$ in the first column denotes singlet(triplet) states. ................................................................. 13

2.3 Optical polarization axes required for the allowed electronic transitions. ................................................................. 15

3.1 The detection efficiency of different optical setups. ... 39

3.2 Tables summarizing the process of the diamond sensor preparation and optimization. ................................. 61

4.1 Superconductor-layer properties measured by the NV sensor. ................................................................. 81
Chapter 1

Introduction

In recent years, nitrogen vacancy (NV) centers in diamonds have been the subject of intensive research, mainly in connection to quantum technology applications [1–10]. In particular, these defects in the diamond lattice were employed as sensitive magnetic [11–16] and electric [17] field probes. Although known for more than 50 years [18], it was only after other atom-like systems such as superconducting Josephson junctions, nuclear magnetic resonance (NMR) devices or quantum dots were suggested for quantum optics applications, that NV centers were applied to the generation of a stable, conveniently manipulated quantum system.

At the heart of most quantum systems stands the ability to define and manipulate a superposition quantum state composed of two basic levels, usually consisting of the internal degrees of freedom of the system. The most straight forward example in this context would be a spin-half configuration of a single particle comprising spin-up and spin-down states. For the majority of applications one has to be able to pump the system into one of these levels, say the spin-up level, and then apply an external field which coherently interacts with the system, placing it in a superposition state of spin-up and spin-down.
The performance of quantum technological devices depends on the coherence of this quantum state which tends to drop due to interaction with the environment (e.g. other quantum states). Hence, systems isolated from their environment, such as cold atoms or trapped ions, were always favorable for the realization of quantum devices. These systems usually have a set of discrete energy levels yielding a spectrum with sharp resonances. The preparation in the initial state is often done using optical pumping techniques, and the manipulation among the two states is carried out using a variety of radiation sources, depending on the energy difference between them. However, the realization of such isolated systems requires expensive and complicated experimental setups involving elements such as ultra high vacuum (UHV) chambers, narrow linewidth lasers and high quality optics. On the other hand, electrons in solid state systems usually have a high degree of coupling to the environment through vibrational degrees of freedom, and their spectral lines are broadened as a result of a fast population redistribution among many levels.

Surprisingly enough, the vicinity of a nitrogen atom and an adjacent vacancy in a carbon diamond lattice, generates a quantum system with both optical and magnetic narrow spectral lines, and a coherence time which exceeds 1 ms, and in special conditions even reaches 1 second [19]. In addition, the system can be easily initialized by optical pumping to a spin level, and may be operated within a simple apparatus and over a wide range of temperatures - from liquid He temperature to high above room temperature.

Consequently, NV centers in diamond have become the basis of many applications and fundamental studies in the field of quantum optics
In particular, magnetic sensing with NV centers suggests a favorable combination of high sensitivity and high spatial resolution.

### 1.1 State of the art

The state of the art of sensitive magnetic sensors is summarized by the diagram in Fig. 1.1. The two axes represent the sensitivity and the minimal detection volume, which are the two main parameters usually accounted for when coming to test a sensor’s performance.

From this diagram we note that magnetometers based on atomic vapors have the highest sensitivity measured [24, 25], but also the lower spatial resolution arising from technical difficulties related to miniature cells fabrication. Furthermore, the maximal sensitivity is achieved at an extremely high temperature (400–500 °C) which is required in order to increase the vapor’s density in the cell. Superconducting quantum interference devices (SQUIDs) [26–28], have also proven themselves able to reach ultra high sensitivity (\( \sim 10 \text{ fT} / \sqrt{\text{Hz}} \)), and were suggested for neurobiology applications. Hall probes [29, 30] have demonstrated lower sensitivity but an impressive spatial resolution making them especially suitable for magnetic measurements close to surfaces of thin films (e.g. imaging of superconducting vortices). Similar to SQUIDs, Hall probes have to be cooled either to liquid nitrogen or liquid helium temperatures, making them less attractive for “out-of-lab” applications. Bose Einstein condensation (BEC) magnetometers [31] exhibit both high spatial resolution and reasonable sensitivity, but the coupling to the probed medium is
extremely challenging as these systems are implemented in a UHV environment.

As reflected by the graph, the higher the sensitivity of a certain method is, the lower is the spatial resolution and vice versa. It is attributed to the fact that most of the sensors are based on quantum spin measurement thereby limited by the quantum projection noise, which is Poissonian by nature. This means the minimal detected field is proportional to $1/\sqrt{N}$, with $N$ being the number of spins\(^1\).

In Fig. 1.1, we highlight this dependency for each sensor by a straight line. These lines assist us in comparing between the different methods. It seems, according to shot noise limit calculations made on real samples [32, 33] (indicated on the graph), that NV related techniques have the potential to compete with the other methods. However the actual performances measured to date (indicated on the graph as well) are still somewhat behind the leading techniques. Finally, NV sensors have a high range of operational temperature ($4-450$ K, approximately), and are relatively cheap and easy to make, comparing to other sensors.

As a result, over the last few years, researchers have developed sensors for scanning magnetometry using nanoscale imaging techniques in bulk diamond [11, 34] as well as in nanodiamonds [21, 35] combined with scanning probe techniques [36, 37]. Sensors employing ensembles of NV centers have even higher sensitivity (as noted it depends on $1/\sqrt{N}$) and the possibility to map out all vector components of the magnetic field [12, 33]. Magnetometers based on NV ensembles have been demonstrated by several groups [13, 38–41].

\(^1\) This dependency serves as a limit; the final sensitivity of a given sensor may be decreased by other factors.
Chapter 1

1.2 Thesis outline

In this thesis we focus on NV ensemble magnetometry which is the method implemented in our lab. Following a discussion of the basic physics of NV centers and the principles of the measurement procedure (Chapter 2), we describe the construction and characterization of a bulk NV sensor made in our lab (Chapter 3). We also demonstrate the disturbance to our sensor caused by fluctuations in temperature. These fluctuations may reduce our magnetic sensitivity considerably. In addition, we describe the effect of light polarization on our signal and suggest ways to apply it for magnetic sensitivity enhancement. Finally, we conclude this chapter by demonstrating the performance of a magnetic sensor developed in our lab. In the

![Figure 1.1: A diagram comparing the various magnetic sensing methods represented by different types of data points (see legend). The reference for each point is denoted beside it. The straight lines represent the approximate trend of the sensitivity with respect to the detector’s volume.](image)
last chapter (Chapter 4), we present an application of a diamond sensor: magnetic sensing of thin filmed high Tc superconductors (HTS). Within the framework of this chapter we describe the preparation of special diamond sensors which are suitable for thin layer probing, their integration with the superconducting sample and results of magnetic field measurements above this structure. In addition we will present a superconducting chip we have fabricated for the future magnetic imaging of vortices, and discuss the expected results.
Chapter 2

Physics of nitrogen vacancy centers in diamond

2.1 Generation of the nitrogen vacancy defect in diamond.

The NV centers are usually hosted in synthetic diamonds\(^1\) fabricated by high-pressure high-temperature (HPHT) procedures or by chemical vapor deposition (CVD) [42]. The result in both cases is a face-centered cubic (fcc) carbon crystal, with the abundance of nitrogen impurities generally being higher in the first process [33]. Hence, the HPHT process is used to obtain a high NV concentration for sensitive magnetometry, while growth by CVD may be used for experiments requiring isolated NV centers.

To generate the vacancies, the synthetic diamonds are irradiated by high-energy particles (\(\sim 0.1 - 5\) MeV), usually electrons or protons [33, 43]. For extremely thin-film NV generation, nitrogen ions are implanted directly on the surface [44] (the energy of the ion beam

\(^1\) NV centers occur also in natural diamonds, but these are rarely used in NV experiments.
usually ranges from several keV to 100 keV). In addition to the particle beam energy, another tunable parameter is the irradiation dose, which determines the density of vacancies generated in the sample.

After irradiation, we anneal the diamonds in an inert atmosphere at $\sim 800 - 900^\circ C$, inducing mobility of vacancies which results in their capture near nitrogen atoms by an attractive potential.

Many studies have been devoted to the preparation process of NV magnetic sensors in order to improve their performance. Among the results are techniques for preferentially orienting the NV [45] and for fabricating isotopically pure $^{12}C$ samples [46]. The latter can result in improved quantum coherence since the less-abundant $^{13}C$ isotope interacts with the NV center. In addition, efforts have been made to increase magnetic sensitivity by enhancing the concentration of NV centers in the lattice [47, 48].

\section*{2.2 $C_{3v}$ group symmetries and the NV structure}

The structure of NV centers is shown in Fig. 2.1(a-b). The nitrogen atom has five electrons in its outer shell, three of which participate in covalent bonds with three carbon atoms. In addition, each one of the three carbon atoms in the vicinity of the NV center has three of four valence electrons participating in covalent bonds. Consequently, there are five available electrons in proximity to the NV complex. However, outer-shell electrons usually achieve greater stability by pairing with another electron, so the odd number of electrons around the NV axis attracts another electron from the lattice and the NV center becomes negatively charged ($NV^-\!$). Although neutrally charged centers ($NV^0\!$) exist in the lattice as well, only $NV^-\!$
centers are used for magnetic sensing, as well as for most other quantum optical applications, and we will henceforth denote this species simply as an NV center. Having two electrons missing to complete the outer shell the defect may be described as a two-holes system [49] whose total electronic spin is zero (a singlet electronic state) or one (a triplet).

The system has $C_{3v}$ symmetry, with three rotations around the NV axis [Fig. 2.1(c)] and reflections with respect to three different symmetry planes [one such plane is shown in Fig. 2.1(d)]. The NV center’s wave functions are classified by their invariance under group elements operations. Mathematically, the group operations can be represented by a set of matrices called a group representation. The irreducible representations (IRs) of the symmetry group are the basic building blocks for each one of the many possible representations. The IRs of $C_{3v}$ are called $A_1$, $A_2$ and $E$. Each one of the system’s wave functions transforms as one of these IRs [50]. The characters of the group elements in all three IRs are shown in Table 2.1.

<table>
<thead>
<tr>
<th>IR</th>
<th>Element</th>
<th>I</th>
<th>$C_3$</th>
<th>$C_3^{-1}$</th>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$R_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 2.1: A character table for the $C_{3v}$ group elements in the different IRs. The elements indicating rotations by $0^\circ$ (360$^\circ$), 120$^\circ$ and 240$^\circ$ are denoted I, $C_3$ and $C_3^{-1}$, respectively. The elements indicating reflections are denoted $R_1$, $R_2$ and $R_3$.

### 2.2.1 Electronic configurations

Prior to the vacancy generation, there were four covalent bonds between the carbon atom, now missing, and its nearest neighbours.
These bonds in the absence of the carbon atom are usually referred to as ‘dangling bonds’ [49]. To describe the defect wave function, we consider a simple model consisting of four $sp^3$ dangling bonds, with three of them associated with the three carbon atoms around the vacancy and the fourth associated with the nitrogen atom. These four bonds are represented by the vectors $\sigma_i$ ($i = 1..4$), and can be projected on each of the group IRs ($A_1$, $A_2$ and $E$) to generate the
single-electron orbital,
\[ \phi_r = P^{(r)} \sigma_i = \frac{l_r}{h} \sum_e \chi_e^{(r)} R_e \sigma_i. \]  \tag{2.1}

Here \( P^{(r)} \) is the projective operator to the IR \( r \), \( l_r \) is the order of the IR \( r \), \( h \) is the number of group elements, \( \chi_e^{(r)} \) is the character of the operation \( R_e \) in the IR \( r \), and the summation is over all the elements of a certain IR.

Introducing the elements of the different IRs into Eq. (2.1) we get two single-electron orbitals \( a_{1'} \) and \( a_1 \), which transform as \( A_1 \), and two degenerate orbitals \( e_x \) and \( e_y \) which transform as \( E \). These single-electron orbitals can now be used to construct the wave functions of the system.

Energetically, both \( a \) orbitals lie beneath the \( e \) orbitals, so they are fully occupied by the four lowest-energy electrons in the ground electronic state, while the \( e_x \) and the \( e_y \) orbitals are only half-occupied by the two remaining electrons. As implied above, this is equivalent to a two-holes description and this configuration is therefore called \( e^2 \).

The two-holes description of the total spatial wave function of the defect is then
\[ \psi_r = P^{(r)} \phi_1 \phi_2 = \frac{l_r}{h} \sum_e \chi_e^{(r)} R_e \phi_1 R_e \phi_2, \]  \tag{2.2}

where \( \phi_{1(2)} \) are single-electron orbitals. Note that two single-particle \( E \) orbitals can form together a wave function which has either \( A_1 \), \( A_2 \) or \( E \) symmetry, so although we do not have a single-electron orbital which transforms as \( A_2 \), we do have a total spatial wave function which transforms as this IR.
The total wave function is a product of the spatial and spin wave functions: $\Psi = \psi_r \Phi$. The spin function $\Phi$ is either a singlet ($S = 0$) or a triplet ($S = 1$). According to the first Hund’s rule [51], the minimum-energy configuration is the one with the two spins co-aligned, i.e. the triplet. Since the Pauli principle requires the total wave function to be anti-symmetric with respect to exchange of particles, the ground state must be the product of an anti-symmetric spatial wave function and a spin triplet (symmetric) [see Fig. 2.2(a) for a schematic view]. Since $A_1$ represents a symmetric orbital, and $E$ represents unstable degenerate orbitals (while experimentally we observe a stable long-lived ground state), the only possible ground state is composed of an $A_2$ orbital and a spin triplet, namely $^3A_2$.

To describe the first excited-state configuration, we promote one electron from the $a_1$ orbital to the $e_x e_y$ orbitals, leaving a hole in $a_1$. The total wave functions are constructed and then ordered energetically as for the ground state configuration $e^2$. There are 8 possible wave functions corresponding to the first excited configuration ($a_1e$), one of which is shown schematically in Fig. 2.2(b). Finally, the spatial wave functions for the two lowest-energy electronic configurations are multiplied by the spin wave functions, as shown in Table 2.2, which also shows the $C_{3v}$ symmetry notation for each of these wavefunctions.

### 2.2.2 Electric dipole transitions

An optical electric dipole transition between $\Psi_i$ in the ground state and $\Psi_f$ in the excited state of the NV system is allowed if the electric
Figure 2.2: (a) The ground state electronic configuration. According to Hund’s rule the spins in both e orbitals are aligned in the same direction. (b) One of the possible wave functions in the first excited configuration, $|a_1e_y|\uparrow\uparrow$.

<table>
<thead>
<tr>
<th>Electronic configuration</th>
<th>$C_{3v}$ state notation</th>
<th>wave function</th>
<th>$m_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_2(T)$</td>
<td>$^3A_2$</td>
<td>$</td>
<td>e_xe_y - e_ye_x\rangle \otimes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$</td>
<td>e_xe_y - e_ye_x\rangle \otimes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$</td>
<td>e_xe_y - e_ye_x\rangle \otimes</td>
</tr>
<tr>
<td>$e_2(S)$</td>
<td>$^1E$</td>
<td>$</td>
<td>e_xe_y + e_ye_x\rangle \otimes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$</td>
<td>e_xe_y + e_ye_x\rangle \otimes</td>
</tr>
<tr>
<td>$ae(T)$</td>
<td>$^3E$</td>
<td>$</td>
<td>a_1e_x + e_xa_1\rangle \otimes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$</td>
<td>a_1e_x\rangle \otimes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$</td>
<td>a_1e_x + e_xa_1\rangle \otimes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$</td>
<td>a_1e_y\rangle \otimes</td>
</tr>
<tr>
<td>$ae(S)$</td>
<td>$^1E$</td>
<td>$</td>
<td>a_1e_x + e_xa_1\rangle \otimes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$</td>
<td>a_1e_y + e_ya_1\rangle \otimes</td>
</tr>
</tbody>
</table>

Table 2.2: Wave functions and $C_{3v}$ symmetries for the electronic configurations $e^2$ and $ae$ of the NV center. The notation $S(T)$ in the first column denotes singlet(triplet) states.
dipole matrix element satisfies

\[ \langle \Psi_f | d \cdot E | \Psi_i \rangle \neq 0, \quad (2.3) \]

where \( d \) is the electric dipole operator and \( E \) is the electric field.

The first selection rule is that \( \Psi_i \) and \( \Psi_f \) should belong to different electronic configurations (i.e., \( e^2 \to ea \)). This is due to the anti-symmetric nature of the dipole operator: it necessarily changes the spatial wave function symmetry. This can be satisfied only if the single electron orbit is changed.

The second selection rule is derived from the \( C_{3v} \) symmetries of the initial and final states compared to the symmetry of the electric dipole. Since the dipole operator is proportional to the position operator \( r \), it is enough to check only for the symmetry of the latter. Assuming the NV axis points in the \( \hat{z} \) direction, this component of the position operator transforms like the \( A_1 \) representation, while the \( \{\hat{x}, \hat{y}\} \) components transform as the \( E \) representation (or, in its components notation, \( \{E_x, E_y\} \)) [50].

For a transition to be allowed, the product \( \Psi_f \otimes (R \otimes \Psi_i) \) must include at least one term which transforms as \( A_1 \), where \( R \) represents the symmetry of the position operator \( (A_1 \text{ or } E) \). To calculate this product we use [50]

\[
A_1 \otimes A_1 = A_1; \quad A_1 \otimes A_2 = A_2; \quad A_1 \otimes E = E;
A_2 \otimes A_2 = A_1; \quad A_2 \otimes E = E; \quad E \otimes E = A_1 \oplus A_2 \oplus E. \quad (2.4)
\]
Table 2.3: Optical polarization axes required for the allowed electronic transitions. We note that the $A_1 \leftrightarrow A_1$ transition is forbidden since it forces the excitation of two single-electron orbitals (from the $e^2$ to the $a^2$ configuration) and $A_2 \leftrightarrow A_2$ is not relevant here since there is only one orbital state of this kind in the system. In addition, the $A_2 \leftrightarrow A_1$ transition is forbidden for either optical polarization due to the symmetry considerations presented in the text.

For example, let us examine the $^3A_2 \rightarrow ^3E$ transition. This transition is allowed via $[\hat{x}, \hat{y}]$-polarized light since $\Psi_f \otimes (R \otimes \Psi_i) = E \otimes (E \otimes A_2) = E \otimes E = A_1 \oplus A_2 \oplus E$. On the other hand, this transition is forbidden using $\hat{z}$-polarized light, since $\Psi_f \otimes (R \otimes \Psi_i) = E \otimes (A_1 \otimes A_2) = E \otimes A_2 = E$. We have used this selection rule to determine the allowed polarization axes for optical transitions between all orbital wave functions, as summarized in Table 2.3.

Since the dipole operator affects only the spatial part of the wave function, and since spin-orbit coupling is weak for these systems, the electron spin is usually preserved for optical transitions. An exception occurs for a three-level $\Lambda$-scheme transition that couples the $m_s = -1$ and $m_s = +1$ spin levels in the ground state $^3A_2$ through one of the two upper levels of the $ae$ configuration with an appreciable spin-orbit coupling. This transition, which is resolvable only at low temperature, has been employed to demonstrate spin-photon entanglement in the NV system [52]. However, under most operating conditions, phonon-induced orbital averaging in the $^3E$ excited state [53–55] or strain shifts in the local environment overwhelm the spin-orbit coupling, and consequently the probability for $\Delta m_s = \pm 1$ transitions is typically < 1% of the allowed transitions.
2.2.3 Photoluminescence spectrum of the NV centers

Both absorption and emission of light for NV centers are highly affected by coupling to the solid lattice. Each one of the electronic states appearing in Table 2.2 is effectively coupled to the vibrational levels of the lattice, and can be described using an harmonic approximation of the Morse potential model [56], as shown in Fig. 2.3(a).

According to the Franck-Condon principle the most probable optical transition is among vibrational levels having overlapped wave functions [57]. The corresponding transition energy depends on the single phonon energy, $\hbar \omega$, and on the number of nearest neighbour sites $n$ through the expression $\Delta E = E_0 + n\hbar \omega$, where $E_0$ is the energy of the electric dipole transition between the ground vibrational levels, usually referred to as the zero phonon line (ZPL). In our system $n = 4$, $\hbar \omega \approx 50$ meV and the ZPL is 1.945 eV (=637 nm). The most probable transition energy thus corresponds to $\sim 570$ nm. However, the phonon side-band absorption spectrum, as shown in Ref. [15], is quite wide around this peak, making the $\sim 532$ nm laser, which is extensively used in spectroscopy, an appropriate choice for the NV excitation source.

Following excitation, the system decays non-radiatively to the lowest vibrational level of the optically excited state, from which it decays radiatively to the ground electronic state. This vibrational relaxation mechanism arises from the much faster phonon decay time ($\sim 1$ ps [58]) compared to the radiative decay time ($\sim 10$ ns [15]).

The emission spectrum of the NV center is composed of a narrow ZPL at 637 nm and a wide phonon side band (PSB) between 650–800
nm [15]. The latter corresponds to transitions between the zero vibrational level of the excited state and all the vibrational levels of the ground state, and its width is attributed to the multiplicity of vibrational modes slightly differed in energy. At room temperature, the fluorescence coming from the PSB emission [Fig. 2.3(b)] nearly obscures the ZPL, but as we cool the system down, the lattice vibrations fade away, and at 4 K we resolve a narrow ZPL which is clearly separated from the PSB [Fig. 2.3(c)].

Figure 2.3: (a) Illustration of the Franck Condon rule via a schematic of the NV system excitation and emission. The vibrational structure is modelled by a simplified harmonic approximation of the Morse potential. The transition corresponding to the highest excitation probability is indicated by the green arrow, while the emission lines are indicated by red arrows. Non-radiative decay is denoted by dashed arrows. (b-c) Photoluminescence spectra of the NV centers (taken from Ref. [59]) at room temperature (b) and at 4 K (c).
2.2.4 Intersystem crossing and optical pumping

Spin-orbit interactions in NV systems mix spin singlets and triplets transforming according to the same IR. This mixing enables transitions between otherwise spin-forbidden singlet and triplet states [60] and is usually referred to as intersystem crossing (ISC). In particular, the relaxation from the $m_s = \pm 1$ spin level in the excited state triplet to the intermediate singlet state opens a non-radiative decay channel to the $m_s = 0$ level in the ground state $^3A_2$. Given that the non-radiative coupling between the $m_s = 0$ level in the excited state and the $m_s = \pm 1$ in the ground state is much weaker [61], and that the radiative transitions are spin-preserving, illumination by continuous green light will pump the population into the $m_s = 0$ ground state.

The non-radiative decay channel, as well as the allowed optical transitions, are shown schematically in Fig. 2.4 [61]. It is important to note that the scheme of the excited state shown here describes the system only for temperatures above $\sim 100$ K, wherein phonon induced transitions among identical spin orbitals practically degenerate the full six $^3E$ levels into three spin projections [54].

Experimental studies of the ISC and the singlet states properties have revealed another optical transition with a ZPL at 1042 nm. This spectral line is attributed to decay among the singlet levels (see Fig. 2.4)\(^2\), and was employed for broadband magnetometry by absorption detection [62].

\(^2\) One may note this optical transition supposedly violates the selection rule according to which the electronic configuration of the initial state must be different from that of the target state (both singlet states belong to the $e^2$ configuration). A possible explanation [49] could be that the NV center is excited non-radiatively, due to spin orbit coupling, from the $^1A_1$ singlet state to one of the singlet states belonging to the $ae$ configuration, and then decays radiatively to the $^1E$ singlet.
Although many experiments have been aimed at finding [61] the exact energy difference between the intermediate singlet levels and the ground triplet state, it still remains unknown. Energy gaps are normally revealed by photon emission detection. However, one has to remember that the electric dipole transition from the singlet states to the ground state is forbidden by selection rules. A second-order transition, even if it exists, would be accompanied by extremely weak fluorescence, and would therefore be much weaker than the relatively fast non-radiative decay process (the lifetime of the singlet states for non-radiative decay is $\sim 150$ ns [63] at room temperature).

2.3 ODMR spectroscopy of the NV ground state and sensitive magnetometry

2.3.1 ODMR spectroscopy

The first demonstration of optically detected magnetic resonance (ODMR) with a single NV center was reported in 1997 [64]. This technique is a powerful tool both for resolving the ground state structure and for magnetic sensing. Prior to this method the most common technique for ground state spectroscopy was electron paramagnetic resonance (EPR). In this method the absorption of a fixed frequency microwave source (usually at $\sim 10$ GHz) is monitored against the variation of an external magnetic field. This method requires extremely high magnetic fields (thousands of Gauss) and sensitive microwave detectors, while ODMR can detect the ground state resonance even in the absence of external fields, and the detection is in the optical regime for which high quantum efficiency photodetectors can be used.
The setup of a typical ODMR experiment is shown in Fig. 2.5(a). The diamond sample is illuminated by green light (\(\lambda = 532\,\text{nm}\)) and its red fluorescence is monitored using a photodetector. A dichroic mirror is used to spatially separate the exciting light from the fluorescence, and a high-N.A. lens or a microscope objective is used for both
focusing the green light and for collecting the fluorescence. Bandpass filters are used to reduce reflections of green light that make their way to the detector. Microwave radiation is usually transmitted by a thin wire attached to the diamond surface.

In the experiment, green light excites the NV centers while the microwave frequency is scanned around the resonance between the $m_s = 0$ and $m_s = \pm 1$ spin levels of the ground state. In the absence of microwave radiation, the green light pumps all the population to the $m_s = 0$ level via ISC, but when resonant, the microwave radiation will repopulate the $m_s = \pm 1$ level. Since the probability for non-radiative processes is much higher for the population in this level, the probability for radiative decay will decrease accordingly, leading to a reduction in the measured fluorescence intensity. This presents itself as a dip in the fluorescence spectrum (as a function of microwave frequency). The shape of this resonance dip will be either Lorentzian or Gaussian depending on the dominant broadening mechanism.

The interaction of the system with external magnetic fields shifts the ODMR resonances in proportion to the field intensity (Zeeman shift), making this method highly applicable for magnetic sensing.

### 2.3.2 The ground state Hamiltonian

The ground state ($^3A_2$) spin levels, $m_s = 0$ and $m_s = \pm 1$ (the $\pm 1$ levels are degenerate in the absence of an external magnetic field and lattice strain), form a two-level system which, as mentioned in
Chapter 1, may have many possible applications to precision measurements and quantum information processing. However, the interaction with external magnetic fields and with the nitrogen nuclear spin complicates the level structure, as shown in Fig. 2.5(b).

The Hamiltonian describing this system consists of $\mathcal{H}_S$ and $\mathcal{H}_I$, the electron and nuclear spin Hamiltonians respectively, and of $\mathcal{V}_{SI}$, the interaction term of these two spins with one another, altogether giving rise to $\mathcal{H} = \mathcal{H}_S + \mathcal{H}_I + \mathcal{V}_{SI}$. The various components are given by

$$
\begin{align*}
\mathcal{H}_S &= DS_z^2 + E \left( S_y^2 - S_x^2 \right) + g_s\mu_B (S \cdot B) \\
\mathcal{H}_I &= PI_z^2 - g_I\mu_N (I \cdot B) \\
\mathcal{V}_{SI} &= A (S \cdot I),
\end{align*}
$$

where $z$ denotes the direction of the NV axis.

The first two terms of the electronic spin Hamiltonian, $\mathcal{H}_S$, describe spin-spin interactions in the NV ground state. The longitudinal part, $DS_z^2$, splits the ground state into the $m_s = 0$ and $m_s = \pm 1$ spin levels, according to the longitudinal zero-field splitting (ZFS) constant of $D \approx 2.87$ GHz. As a result of local strain in the lattice [53], there is also a transverse spin-spin interaction which splits the zero-field resonance according to the off-diagonal term $E \left( S_y^2 - S_x^2 \right)$. The value of the transverse ZFS constant $E$ varies among samples, but does not exceed several MHz even in a highly perturbed sample [64] [e.g., see the spectrum in Fig. 2.5(c)].

An external magnetic field $B$, applied to the NV center, shifts the energy of the spin levels according to their spin projections. This

---

3 For this constant, as well as other constants in the Hamiltonian, which should have units of energy, we ignore the Planck constant and give the values in units of frequency.
shift (Zeeman shift) is related to the magnetic field via

$$\Delta \nu_z = m_s g_s \mu_B (S \cdot B),$$

(2.6)

where $g_s = 2.003$ [65] is the Landé factor and $\mu_B = 1.4$ MHz/G is the Bohr magneton. The magnetic field intensity may be extracted from measurements of this frequency shift [see Fig. 2.5(d)]. Since the spin of the NV system is aligned with the NV axis ($=\hat{z}$-axis), only the field projection along this axis is sensed by the NV center. Hence, we may employ an ensemble of defects, comprising all four possible NV orientations, for a vectorial measurement of the magnetic field.

Measurements show that the nitrogen atom nuclear spin structure also affects the location of the ODMR resonances [66]. The energy levels of the NV center are split and shifted due to spin-spin nuclear interactions according to $PI_z^2$, and due to an external magnetic field according to $-g_I \mu_N (I \cdot B)$. The value of the quadrupole term is $P = -4.95$ MHz [66, 67], while the values of the Landé factor and the nuclear magneton are $g_I = -0.416$ [65] and $\mu_N = 0.76$ kHz/G, respectively. It is clear from these numbers that the spin-spin interaction induces a visible splitting between the $m_I = 0$ and $m_I = \pm 1$ nuclear spin levels\footnote{Since the natural abundance of the $^{14}$N isotope in diamonds is $\sim 99.6\%$ compared to $\sim 0.4\%$ for $^{15}$N, the level diagram shows only the splitting induced by $^{14}$N with its nuclear spin of $I = 1$ (the nuclear spin of $^{15}$N is $I = 1/2$).}, while the magnetic shift of the energy due to the nuclear spin is negligible.

The interaction between electronic and nuclear spins further splits the energy levels as demonstrated in Fig. 2.5(b). The magnitude of the interaction is given by the hyperfine tensor $A$. In our case, due to its axial symmetry, the interaction term can be rewritten as $V_{SI} = A_\parallel S_z I_z + A_\perp (S_x I_x + S_y I_y)$, where $A_\parallel \approx 2.16$ MHz [66]
and $A_\perp \approx 2.70 \text{MHz}$ [65] are the axial and transverse components of the hyperfine tensor, respectively. In Fig. 2.5(e) the splitting of an ODMR resonance due to the interaction with the nuclear spin is demonstrated. Note that both here and in Fig. 2.5(b) we assume an axial external magnetic field, hence the energy shift of the levels depends only on the component $A_\parallel$ of the hyperfine tensor $A$.

### 2.4 NV magnetometry

Static magnetic field sensing with NV centers, in its simplest form, is based on ODMR spectroscopy. The magnetic field is calculated using the two resonances in the spectrum $\nu_+$ and $\nu_-$ corresponding to the $|m_s = 0\rangle \rightarrow |m_s = +1\rangle$ and $|m_s = 0\rangle \rightarrow |m_s = -1\rangle$ transitions [see Fig. 2.5(d) for examples]:

$$B_z = \frac{\nu_+ - \nu_-}{2g_s \mu_B}. \quad (2.7)$$

We denote the field by $B_z$ since, as we have explained above, only the field projection along the NV axis ($=\hat{z}$-axis) is measured with this technique.

The smallest field detectable by such an optical measurement is given by [68]

$$\delta B = \frac{\delta S}{dS/dB}, \quad (2.8)$$

where $S$ is the signal measured in the experiment, $\delta S$ is its standard deviation, and $dS/dB$ is its slope with respect to the magnetic field. To calculate the shot-noise limited $\delta B$ for the ODMR fluorescence signal, we assume a natural linewidth for each one of the dips in the spectrum, namely $\delta \nu_{+(-)} = g_s \mu_B dB \approx 1/\pi T_2^*$, where $T_2^*$ is the ensemble coherence time. Due to the quantum nature of
Figure 2.5: (a) Typical setup for an ODMR experiment. See details in the text. (b) An illustration of all levels arising from interactions splitting the ground state, in the presence of an axial magnetic field. The energy splittings are expressed in terms of the hyperfine constants whose typical values are given in the text. Allowed transitions are indicated by double arrows. Electronic and nuclear spin projections are denoted by $m_s$ and $m_I$, respectively. (c) An ODMR spectrum measured at approximately zero magnetic field. The experimental results are fitted to a double-peak Lorentzian (solid red). The measured splitting of $\sim 5$ MHz is related to the transverse spin-spin interaction, which is induced by lattice strain splitting of the $\pm 1$ levels. Note that the splitting energy is $2E$. This result is obtained by diagonalizing the transverse spin-spin interaction term $E (S_y^2 - S_x^2)$. (d) A demonstration of the splitting in the spectrum induced by a magnetic field. The different spectra are for different magnetic fields. (e) Splitting of an electronic spin transition as a result of interactions between the NV center and the $^{14}$N nucleus in the presence of an axial magnetic field. The frequency separation between dips is expressed using the hyperfine constant $A_\parallel$. This constant was measured from the spectrum to be $A_\parallel = 2.07 \pm 0.21$ MHz which is in an agreement with the reference value given in the text ($A_\parallel = 2.16$ MHz).

The measurement, $\delta S = \sqrt{N} \sqrt{m} = \sqrt{N} \sqrt{t/T_2^*}$ where $N$ is the number of spins, $m$ is the number of measurements, and $t$ is the measurement time. Adding an “experimental” constant $C$ (ranging from 0 to 1) to account for attenuations in sensitivity, we also
get \(dS = CNm = CN(t/T_2^*)\). Introducing all of the above into Eq. (2.8) we obtain

\[
\delta B \approx \frac{1}{C g_s \mu_B} \times \frac{1}{\sqrt{NT_2^*} t}.
\] (2.9)

The experimental constant is 

\[C = R \sqrt{\eta}, \]

where \(R\) is the signal contrast defined as the resonance depth and \(\eta\) is the photon detection efficiency. The contrast \(R\) is limited by the amount of \(m_s = \pm 1\) population in the excited state that undergoes the ISC process compared to the population undergoing radiative decay. In dilute samples (low nitrogen concentration) the contrast may reach 30\% [37, 69]. Since the refractive index of diamond is relatively high \((n \approx 2.4)\), ODMR experiments have usually suffered from low detection efficiency \((< 1\%)\). Many methods to overcome this have been developed over the years, some of which have reached impressive efficiency, such as “side-collection” [41] and solid immersion lens fabrication of the diamond itself [70, 71]. Such methods have brought the collection efficiency record to just under 50\% and, thereby, the optimal experimental constant \(C\) to nearly 0.2.

Another parameter of great importance to the sensitivity is the ensemble coherence time, \(T_2^*\), which is mainly affected by the interaction of the NV center with its environment. In particular, interactions with the \(^{13}\)C isotope, whose nuclear spin is \(I = 1/2\) and whose natural abundance is \(1\%\), is a major decoherence factor. Recently, samples with an extremely high concentration \(\sim 99.99\%\) of the zero-spin \(^{12}\)C isotope were prepared, increasing the ensemble coherence time by about two orders of magnitude [46]. Interactions with the electrons of other nitrogen atoms in the lattice also reduces the coherence [72]. This issue is usually addressed by using dilute
samples. In the case of an ensemble, one also finds inhomogeneous broadening due to local strains in the lattice and magnetic field gradients.

Finally, a coherence time $T_2^* \approx 100 \mu s$ is certainly achievable using isotopically pure $^{12}$C diamonds. Moreover, AC magnetometery has been performed using spin echo techniques that effectively decouple the defect from its environment, making the figure of merit $T_2$. In a low-temperature environment, $T_2$ approaching 1 s has been reported recently [19].

2.4.1 Ensemble NV magnetometry

So far in this chapter, we have discussed NV physics in general, and presented basic spectroscopy and magnetometry features which are relevant for both a single NV center and an ensemble of NV centers. There are however, a few features connected to the ensemble system, compared to a single defect, that place it in a favorable position as a magnetic sensing system. Historically, single-NV magnetometers were first demonstrated exhibiting sensitivities as high as $100 \, \text{nT}/\sqrt{\text{Hz}}$ in a $\sim 10^{-23} \, \text{m}^3$ detection volume [12]. From Eq. (2.9), it is clear that ensemble magnetometry can potentially increase the sensitivity since it is proportional to $1/\sqrt{N}$. As confirmation, a sensor with a shot-noise limit of $10 \, \text{pT}/\sqrt{\text{Hz}}$ was recently demonstrated [32]. Introducing the optimal values given above for $C$ and $T_2^*$ to Eq. (2.9), as well as $N = 10^{10}$ NV centers\(^5\), we find an even better sensitivity, namely $\delta B \approx 30 \, \text{fT}/\sqrt{\text{Hz}}$ for a $10 \times 10 \times 100 \, \mu \text{m}$ sensor.

\(^5\) Such a number of NV’s can potentially be gathered in a volume of $10^{-14} \, \text{m}^3$, amounting to a 10 ppm NV concentration, which is the concentration reported in Ref. [32]
In addition, the ensemble sensor enables a vectorial detection by monitoring the field projection on each one of the four possible NV orientations given, in the crystal coordinates, by \([1,1,1], [\bar{1}, \bar{1}, 1], [\bar{1}, 1, \bar{1}], [1, \bar{1}, \bar{1}]\). Diamonds are usually cut along one of the three crystallographic planes, \{100\}, \{110\} and \{111\}. Assuming the magnetic field is perpendicular to the diamond surface, the corresponding directions of the magnetic field in the lattice coordinates are \([1,0,0]\), \([1,1,0]\) and \([1,1,1]\), respectively. The spectrum obtained for each case is shown in Fig. 2.6. In the \{100\} diamond [the magnetic field is perpendicular to the diamond facet, Fig. 2.6(a)] all four NV orientations experience the same magnetic field projection, and consequently the corresponding resonances remain degenerate. When the field is aligned along the \([1,1,0]\) axis [Fig. 2.6(b)], two of the orientations are 35° to it, while the other two orientations are perpendicular to the field axis and are thereby insensitive to its intensity (the observed small splitting is due to strain). The \{111\} diamond [Fig. 2.6(c)] is perhaps most advantageous for magnetometry, as the field is co-aligned with one of the NV orientations leading to a non-degenerate resonance in the spectrum. The other three NV orientations sense identical and rather weak field components.
Figure 2.6: Magnetic field orientations and the corresponding ODMR spectra for the three possible crystallographic planes: (a) \{100\}, (b) \{110\} and (c) \{111\}. In all crystal structure images the magnetic field is perpendicular to the image plane. The gray spheres represent carbon atoms, the blue ones are for nitrogen atoms and the red spheres denote vacancies. The ODMR spectrum in (c) is done with a smaller number of experiments being averaged and hence exhibits noisier data. In (c) we also show the Lorentzian fit as an example. This fit will be discussed again in later chapters.
Chapter 3

Characterization and optimization of NV sensors

In this chapter we describe the construction and performance of magnetic sensors based on NV ensembles in our lab. In Sec. (3.1) we give a detailed overview of the various components of the experimental system, from the optical setup, through diamond samples preparation, to signal processing. Section (3.2) is devoted to the comprehensive study of the change in the ZFS constant due to temperature fluctuations. This change, as we show here, induces a significant perturbation to the sensor performance. Next, in Sec. (3.3), we describe the effect of the green light polarization on the ODMR spectrum. A theoretical analysis is followed by experimental results and a discussion regarding the possibility of utilizing this effect to decrease the ODMR resonance linewidth. In the last section of this chapter we summarize this work by presenting the performance of a magnetic sensor constructed in our lab. In addition, we compare the measured sensitivity of our sensor to the shot-noise limit and analyze noise sources which need to be suppressed in order to reach this limit.
3.1 Experimental technique

The experimental system is illustrated schematically by the block diagram in Fig. 3.1. The ODMR optical setup [already described generally in Sec. (2.3.1)] is depicted in the inset.

![Diagram of the experimental system](image)

**Figure 3.1:** A diagram of the experimental system. The solid black lines represent electrical connections. The red arrows denote the fluorescence emitted by the NV’s, collected, collimated, filtered by the optical setup, and detected by the photodiode. All abbreviations used in the figure are defined at the bottom. The inset shows details of the framed part.

The green light source in our system is a diode-pumped solid state laser (maximal power of 150 mW) manufactured by Aixiz. A dichroic mirror fabricated by Chroma (99.9% reflection at 532 nm) reflects this light and a microscope objective (Olympus Pro-Plan, magnification ×40; N.A. = 0.65; working distance = 2.4 – 4 mm) is used to focus it on the diamond. These two elements were mounted on a
custom-made cube to maintain optical alignment. The red fluorescence emitted in the decay process of the NV’s is collected by the same objective and focused on the photodiode using a second lens. For fast detection, required especially for monitoring Rabi oscillations, we used an avalanche photodiode from Thorlabs (APD110A) having a bandwidth ranging from DC to 150 MHz; otherwise a narrow-band photodiode (DET210) was used. For additional filtering of scattered green light we used band-pass and/or high-pass filters from Semrock.

The microwave power is transmitted using a $\sim 100 \, \mu m$-thick wire stretched along the center of the diamond plate. The field distribution in the immediate proximity of the wire is rather uniform and is given by $B[G] \approx \frac{2[I[A]}{r[mm]}$. Microwave power reflected by the wire is measured by connecting a directional coupler between the microwave generator and the wire and sending its output to a power spectrum analyzer (Rhode and Schwartz Model FP13). To measure the power dissipated on the wire, we connect the directional coupler on the other end of the wire and subtracted the reflected power from the result obtained. The microwave signal itself is produced by an Agilent signal generator (Model E4426B ESG-AP) and amplified by a Mini-Circuit amplifier (Model ZHL-16W-43+) whose maximum output is 16 W.

The diamond plates we have used were all fabricated in an HPHT process and had an initial nitrogen concentration of $\sim 100$ ppm. Their thickness is $500 \, \mu m$ and their size is $3 \times 3$ mm. They were
irradiated by our collaborators from Berkeley using a 3 MeV electron beam with a dose ranging from $10^{17}$ to $10^{18}$ cm$^{-2}$. Such diamonds are especially suitable for applications requiring high sensitivity, since they all have a rather high number of NV defects. In Chapter 4 we describe the preparation of other diamond sensors having a thin layer of NV’s ($\sim 10$ nm compared to 500 $\mu$m here) which are especially suitable for thin-film magnetic imaging. The diamond annealing which generates the NV centers was done in an inert atmosphere at 850°C for three hours. The resulting NV concentration was estimated by photoluminescence measurements. Relevant properties of the diamond tested are summarized in a table at the end of this chapter [Table (3.2)].

In the experiment we scan the microwave frequency while illuminating the sample with green light. The signal generator provides a voltage ramp, proportional to the microwave frequency, which is used to trigger the scope. We save both the voltage ramp and the ODMR image in files using a LabView program, and then processes the data in Matlab to obtain a graph of the normalized fluorescence vs. the microwave frequency. Our LabView program also enables averaging up to 128 images for noisy spectra.

As frequently done in spectroscopy, we use the lock-in technique to filter high-frequency noise, thereby increasing the signal-to-noise ratio (SNR). Frequency modulating the ODMR signal, and mixing it with the modulation wave in a lock-in amplifier, we obtain an error signal which is effectively the derivative of our ODMR spectrum [73].

The frequency modulation (FM) signal is

$$S_m = V_m \cos [\omega_e t + (\omega_\Delta/\omega_m) \cos (\omega_m t)],$$  \hspace{1cm} (3.1)
where $\omega_c$ is the carrier frequency. The rest of the parameters are determined by considering the ODMR signal features. The FM depth, $\omega_\Delta$, is usually tuned to be of the same order as the ODMR resonance linewidth. Scanning over the relevant range we have found that a modulation depth of 6 MHz is a suitable choice under our experimental conditions; however, a change of $2 - 3$ MHz does not affect the resulting error signal significantly. The modulation frequency, $\omega_m$, is usually tuned to the lowest value possible, since noise with higher frequencies is filtered by the lock-in amplifier. Empirically, we have found that $\omega_m \approx 500$ Hz gives a low-noise signal with a high amplitude. The output signal of the lock-in amplifier is basically a product of the optical and modulation signals (integrated over time). Thus, the modulation amplitude, $V_m$, is usually set to a much higher value compared to the signal amplitude, leading to a high amplification. In our system we generally work with $1 - 2$ V.

In addition, the knobs of the lock-in amplifier itself must be tuned carefully: the lock-in sensitivity is usually taken to the maximum possible, just below the overload point, to utilize its amplification to the fullest. The integration time constant must be optimized by ensuring that variations in the optical signal will be noticeable. Adjusting the phase is a matter of convenience: the lock-in amplifier has two output channels differing in phase by $\pi/2$ (denoted as the x and y channels), from which all the relevant information can be extracted and processed afterwards to maximize the amplitude of the error signal. However, in order to maximize the amplitude “in situ”, one may adjust the phase between the optical and reference signals directly on the lock-in amplifier by maximizing one channel while getting the other channel as close to zero as possible.
3.1.1 Optimization of the ODMR setup

In the previous chapter we have discussed how the properties of the diamond sample affect the final magnetic sensitivity. However, the probing system itself, and all its components, must be tuned properly to achieve the fullest performance for a given sample.

For example, raising the microwave power above a certain value leads to power broadening of the ODMR resonance and thereby decreases the magnetic sensitivity. The behavior of the linewidth with respect to the microwave power in our system is exhibited in Fig. 3.2. We have resolved the NV orientations by applying a magnetic field, while monitoring one of the ODMR resonances. The linewidth is extracted from Lorentzian fits to the spectrum. It is clear from this graph that the signal is power broadened starting at $\sim 0 \text{ dbm}$ (all the values noted here are before amplification), making this an ideal value to work with since it maximizes contrast while preserving the natural linewidth of the transition which depends only on the sample properties.

Surprisingly, the power of the green laser light has the opposite effect on the resonance width. Increasing the power of the green light reduces the ODMR linewidth [32]. The reason is that the green light we use to probe the population also pumps it continuously to $m_s = 0$. As the laser power is raised this pumping is enhanced, effectively lengthening the longitudinal coherence time $T_1$. This reduces the linewidth, as can be seen in Fig. 3.3. Note that the fluorescence becomes saturated at some point, as shown in the figure’s inset, and from this point on, the ODMR linewidth is broadened.
As mentioned in Chapter 2, the photon detection efficiency is also a key parameter for magnetic sensitivity enhancement. Thus, we have tested several optical configurations in order to optimize it in our system. The collection efficiency is given by

$$\eta \approx \frac{P_r \bar{\lambda}_r}{Q P_g \lambda_g},$$

(3.2)

where $P_r$ and $P_g$ are the powers of the red fluorescence and the green light respectively, $\lambda_g = 532\text{ nm}$ is the green light wavelength, $\bar{\lambda}_r \approx 700\text{ nm}$ is the average wavelength of the fluorescence, and $Q$ is the quantum efficiency of the detector. For each configuration we have plotted a graph of the emitted fluorescence vs. the green laser power. We have extracted the collection efficiency from the linear fit of this graph (see illustration in the inset of Fig. 3.3).

The four configurations we have tested are shown in Fig. 3.4. The first configuration [Fig. 3.4(a)] utilizes a multimode optical fiber,
Figure 3.3: Laser narrowing of the ODMR spectral line. Two ODMR spectra taken with different laser power are shown. In the left inset the full width at half maximum (FWHM) of the ODMR signal as a function of the laser power is presented. The linewidth is clearly decreased as the laser power is increased. In the right inset we show the dependence of the fluorescence on the laser power. We also demonstrate the calculation of fluorescence detection efficiency $\eta$ using a linear fit to the data, where $\Delta P_f$ is the change in the fluorescence power with respect to a change ($\Delta P_g$) in the excitation power [this is just an approximation and the exact formula is given in Eq. (3.2)].

both for transferring the green light to the diamond, and for collecting the emitted red fluorescence. The detection efficiency of the fiber configuration was measured to be 0.03%. This low efficiency may be explained by the relatively low N.A. of the fiber. Nevertheless, this method makes the expensive optical elements usually used in ODMR setups redundant. Hence, it may be used in cases for which cost is more important than high magnetic sensitivity, e.g. for an array of sensors.

Next, we have tried to enhance the collection efficiency by using an integrating sphere (made by Thorlabs; model IS200). In this configuration we expect that besides photons that fly directly to the
detector, additional photons will be detected after reflection from
the sphere’s walls, as sketched in Fig. 3.4(b). This method yielded
a rather disappointing collection efficiency of 0.04%. Since we do
not use any collimating elements for the fluorescence, as we do in
the other configurations (clearly, we cannot place lenses inside the
sphere), the collection efficiency depends solely on reflections within
the integrating sphere that are apparently insufficient in this case.

The maximum collection efficiency, more than 5%, was achieved
using large photodiodes placed on both sides of the diamond [see
Fig. 3.4(c)]. However, in this configuration, we cover almost the en-
tire area of the fluorescence emission, blocking access to the diamond
almost completely and preventing us from setting up other elements
necessary for the ODMR spectroscopy, such as the microwave trans-
mission wire. In addition, this configuration is inapplicable in low
temperature experiments where the diamond is placed in a cryostat.

Finally, we have used a microscope objective [see Fig. 3.4(d)], both
for focusing the green light and for collecting the red photons. The
collection efficiency in this configuration was 0.26% and we used this
configuration for all our subsequent experiments. The results of our
collection efficiency measurements are summarized in Table 3.1.

As an outlook we suggest the use of AR coated diamonds for ODMR
spectroscopy. This coating will reduce the internal reflections of
fluorescence inside the diamond which are due to its relatively high
index of refraction ($n \approx 2.4$).
<table>
<thead>
<tr>
<th>No.</th>
<th>Method</th>
<th>( \eta [%] )</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Optical fiber</td>
<td>0.03</td>
<td>Multi-mode fiber, core size: 62.5 ( \mu )m.</td>
</tr>
<tr>
<td>2</td>
<td>Integrating sphere</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Two large photodiodes</td>
<td>5.67</td>
<td>Sensor active area is 1 ( \text{cm}^2 )</td>
</tr>
<tr>
<td>4</td>
<td>Microscope objective</td>
<td>0.26 ×40 magnification; 4 mm working distance</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1: The detection efficiency of different optical setups.

### 3.1.2 Rabi spectroscopy

The population of a two-state system initially prepared in the lower state, and then subjected to resonant (or slightly detuned) radiation, will undergo oscillations between the two states, usually referred to as Rabi oscillations [74]. The resonant Rabi frequency, \( \Omega_0 \), is proportional to the radiation intensity, and as we detune the radiation frequency from resonance, the frequency of the oscillations increases while their amplitude decreases. The decay of the Rabi oscillations over time is characterized by the ensemble coherence time \( T_{2}^{*} \). Hence, monitoring the Rabi oscillations may provide us with information regarding the coherence of our system, and the actual radiation power experienced by the NV centers.

We therefore probed the Rabi oscillations in our system between the \( m_s = 0 \) level and one of the \( m_s = \pm 1 \) levels (separated by an external magnetic field). In the experiment, the diamond is illuminated constantly by green light at low power, which has a weak pumping effect but which still induces fluorescence proportional to the spin state population. Peak fluorescence corresponds to concentrating all the population in \( m_s = 0 \), while minimum levels of fluorescence correspond to full population transfer to \( m_s = -1(+1) \). We simultaneously apply short microwave pulses (\( \sim 5 \mu s \)) with a duty cycle

\(^1\) This is not exact but a reasonable approximation for weak driving [75].
of $\sim 1\%$ (see the inset in Fig. 3.5). As a result of the short duty cycle and of the low laser power, the system is pumped to the $m_s = 0$ level when the microwave power is off, and undergoes Rabi oscillations when it is on. Synchronizing the scope with the microwave pulse displays the evolution of the oscillations on our screen.

In Fig. 3.5 the Rabi oscillations between $m_s = 0$ and $m_s = -1$ are shown (blue data points). The detuning of the microwave frequency
in this case is approximately zero in order to maximize the amplitude of the oscillations. We fitted the experimental data to

\[ f(t) = A \left( 1 - \frac{1}{2} \cos \Omega t \right) e^{-t/T_2^*}, \tag{3.3} \]

where \( A \) is the amplitude of the oscillations, \( \Omega \) is the Rabi frequency, and \( T_2^* \) is the ensemble coherence time. Parameters extracted from the fit are \( \Omega = 2.15 \pm 0.13 \text{ MHz} \) and \( T_2^* = 0.57 \pm 0.04 \mu \text{s} \).

![Figure 3.5: Room temperature Rabi oscillations between the \( m_s = 0 \) and \( m_s = -1 \) levels. An exponentially decaying cosine is fit to the data points. The fit parameters are indicated on the graph. In the inset, a diagram of the experimental sequence is shown.](image)

3.2 Temperature dependence of the ODMR signal

3.2.1 Background and motivation

Uncertainty in magnetic field measurements comes not only from the quantum fluctuations which are dominant on short time scales (the
ensemble coherence time, $T_2^*$), but also from signal drifts occurring on a much longer time scale. The main mechanism relevant in this connection is the variation of the longitudinal ZFS constant, $D$ [see Eq. (2.5)], due to temperature fluctuations. According to the results presented herein, a variation on the order of $\sim 80$ Hz is expected in the frequency of the magnetic ODMR resonance as a result of a $1\text{ mK}$ temperature fluctuation. This corresponds to a $\sim 3\text{ nT}$ drift in the magnetic sensor reading, which is quite considerable in terms of sensitive magnetometry (e.g., it is on the order of the magnetic field expected from a single neuron firing [76]).

The analysis of $D$ variations produced by temperature changes is therefore a necessary first step in overcoming long-term drifts in diamond magnetic sensors. Here we conduct an experimental study of $D$ over a wide range of temperatures, from 10 to 330 K. We analyze the results and discuss their influence on diamond magnetometry.

Some of the work presented in this section was done at the University of California, Berkeley as part of a collaboration with the lab of Professor Dmitry Budker. The work carried out in Berkeley included measurements over a more modest temperature range of $280 - 326$ K and the theoretical calculation of $D$. All measurements in the cryostat were performed in our lab at Ben Gurion University.

### 3.2.2 Calculation of $D$

The origin of $D$ is expected to be predominately due to dipolar spin-spin coupling between the two electron-holes forming the NV center. Thus, a likely reason that $D$ changes with temperature is lattice expansion. Denoting the distance between the two spins by $r_{12}$ and
assuming that they are both aligned along the N-V symmetry axis, the average spin-spin interaction term is

\[ \langle V_{ss} \rangle = \langle (r_{12} - 3z_{12}) / r_{12}^5 \rangle, \]  

(3.4)

where \( z_{12} \) is the projection of \( r_{12} \) on the N-V axis. Next, the temperature derivative of \( D \) is calculated by

\[ \frac{dD}{dT} \approx \frac{d\langle V_{ss} \rangle}{dR} \frac{dR}{dT}, \]  

(3.5)

where \( R \) is the distance between the basal carbon atoms and \( \frac{dR}{dT} \) is the thermal expansion coefficient. Assuming the spins are localized near the carbon atoms [77, 78] and introducing \( R = 0.252 \text{ nm} \) and \( \frac{dR}{dT} = 0.252 \cdot 10^{-5} \text{ nm/K} \) [79] into Eq. 3.5, we get a value for \( dD/dT \) which is 4.5 times the experimental value measured in this work. Moreover, integrating the equation yields \( D = 2.66 \text{ GHz} \) at room temperature, which is about 20 MHz lower than the known experimental value. These disagreements suggest that macroscopic thermal expansion is not a good description of \( dR/dT \) in the vicinity of the defect. \textit{Ab initio} calculations [51, 77, 80] that include the determination of local thermal expansion effects are needed to give a more accurate prediction of \( dD/dT \).

3.2.3 Experimental results

The experimental method for measuring \( D \) and \( E \) [see Eq. (2.5)] is presented in Fig. 3.6. The system used here consists of the standard ODMR setup described earlier in this chapter. In the experiments performed in the Berkeley lab, we controlled the temperature to a resolution of 0.01 K using a PID loop and a thermoelectric cooler (TEC) attached to the diamond mount. In the Ben Gurion
lab we used a commercial cryostat (Janis ST-500) with a temperature resolution of 0.02 K. No external field was applied for any of the measurements, and we used compensation coils to zero the Earth’s field. However, we take into account that a small residual field remains, since no magnetic shielding was used.

We summarize the results taken at Berkeley in Fig. 3.7. Two ODMR spectra at the different temperatures exhibited in Fig. 3.7(a) show a clear variation of $D$. In Fig. 3.7(b) we show the change in $D$, calculated from the ODMR fit (as shown in Fig. 3.6), with respect to the temperature. In this range, a clear linear dependence is observed and, specifically for the diamond tested here, the temperature variation coefficient obtained is $dD/dT = 76(2) \text{ kHz/K}$, corresponding to a magnetic field error of $\sim 3 \text{ nT}$ for a 1 mK temperature deviation.
As opposed to $D$, the splitting $E$ does not show any clear dependence on temperature. From the graph in Fig. 3.7(c) we conclude that $E$ fluctuates randomly around an average value of $\sim 5.9 \text{ MHz}$ without any correlation to the temperature. We relate these $\sim 100 \text{ kHz}$ fluctuations mainly to small changes in the ambient magnetic field (a $100 \text{ kHz}$ deviation of $E$ corresponds to $\sim 20 \text{ mG}$ in the magnetic field, which is perfectly reasonable given that we have no magnetic shielding).

A more complex behavior of the ZFS longitudinal constant is revealed by measurements over a wider range of temperature, as shown by Fig. 3.8. At around 100 K, $D$ reaches a maximum value and remains approximately constant as the temperature drops further to 10 K. This result, which is in agreement with both theory and other experiments [81], substantiates our prior assumption [given in Sec. (3.2.2)] that $D$ changes due to lattice expansion, which normally
relaxes at such temperatures (the exact value depends on the specific lattice structure).

In Ref. [79], the lattice parameter of a synthetic diamond was measured vs. temperature and a dependence of $\approx T^5$ was found. Assuming a similar temperature dependence for $D$ we fitted the experimental data by a fifth-order polynomial, namely,

$$D = \sum_{l=0}^{5} d_l T^l,$$

where the optimized fit coefficients are $d_0 = 2877 \text{ MHz}$, $d_1 = -1.7 \times 10^{-2} \text{ MHz/K}$, $d_2 = 2.5 \times 10^{-4} \text{ MHz/K}^2$, $d_3 = -1.5 \times 10^{-6} \text{ MHz/K}^3$, $d_4 = 6.2 \times 10^{-9} \text{ MHz/K}^4$, and $d_5 = -7.8 \times 10^{-12} \text{ MHz/K}^5$. These results are in reasonable agreement with Ref. [81].
3.3 Polarization-selective excitation

3.3.1 Background and motivation

As mentioned in Sec. (2.2.2) the dipole interaction matrix element describing the probability of the NV center electronic excitation from the $^3A_2$ ground state to the $^3E$ excited state, is nonzero only if the light is polarized perpendicular to the NV symmetry axis. In other words, the excitation probability depends on the angle between the NV symmetry axis and the polarization vector. By polarizing our light in a certain direction, we may selectively excite only certain NV orientations. This can potentially be applied to obtain a non-degenerate (or a partly-degenerate) ODMR spectral line even in the absence of an external magnetic field, which is usually used to resolve the orientations.

For convenience, let us define two working coordinate frames: the first one is the frame associated with the NV orientation $i$ ($i = 1 \ldots 4$), wherein a coordinate is denoted $(x_i, y_i, z_i)$, and the NV symmetry axis lies along the $\hat{z}_i$-axis. The second one is the frame of the laser beam, wherein a coordinate is denoted $(x', y', z')$, and the $\hat{z}'$ axis is the wave propagation direction (i.e., the $k$-vector), which is fixed to be perpendicular to the diamond surface. The light polarization plane is therefore parallel to the $x'y'$ plane.

For light propagating along the NV symmetry axis ($z_i \parallel z'$), the two frames we have defined coincide, leading to a maximum excitation probability, $P_0$, independent of light polarization. Assuming the fluorescence intensity obtained in this case is $I_0$, for any other
configuration the fluorescence $I$ would be \[ I = I_0 \left( \sin^2 \phi_i + \cos^2 \theta_i \cos^2 \phi_i \right), \] (3.7)

where $\theta_i$ is the angle between the polarization vector $\mathbf{E}$ and its projection on the $x_iy_i$ plane, $\mathbf{E}_i$. The angle between $\mathbf{E}_i$ and the $x_i$ axis is denoted $\phi_i$. The axis $y_i$ is defined as the vector which exists in both planes (i.e. the crossing between the two planes). The angles and vectors are illustrated in Fig. 3.9(a). It is easy to show that $\theta$ is also the angle between $\mathbf{z}'$ and $\mathbf{z}_i$, namely between the light propagation axis $k$ and the NV axis.

While $\phi_i$ depends on the light polarization angle, $\theta_i$ is determined only by the NV orientation. Given the crystallographic plane the specific diamond is cut along (\{111\}, \{110\} or \{100\}), we can find $\theta_i$ for each NV orientation and predict the influence of the polarization angle on the spectrum. For example, for a \{111\} diamond, one of the NV-axes, hereby denoted NV1, is co-aligned with the $k$-vector of the light, hence the excitation probability is maximal regardless of the polarization angle [see Fig. 3.9(b)]. The other NV-axes (NV2, NV3, and NV4) make an angle of $\theta = 109.5^\circ$ with the $k$-vector, so Eq. (3.7) becomes

$$ I = I_0 \left( \sin^2 \phi_i + \frac{1}{9} \cos^2 \phi_i \right). $$ (3.8)

Note that there is a phase difference of $60^\circ$ between the curves representing the three NV orientations, due to the $C_{3\nu}$ symmetry, as shown in Fig. 3.9(b).
Figure 3.9: Theory of polarized excitation. (a) The laser and the defect coordinate frames. The three carbon atoms, the nitrogen, and the vacancy are marked by gray, blue, and red spheres respectively. The solid white lines define the NV frame, while the solid green lines define the laser frame. The wave ($k$) and polarization ($E$) vectors are denoted in the laser frame. $E_i$ is the projection of the polarization vector on the NV frame. The angles $\theta$ and $\phi$ are defined in the text. (b) Plots of Eq. (3.7) for the four different NV orientations in the $\{111\}$ configuration.

3.3.2 Experimental results

Our first goal was to verify Eq. (3.8) experimentally. For this purpose we used the same conventional ODMR setup with two modifications: we put a polariser in the green beam path (the light at the laser output is unpolarized), and we inserted a half-wave plate (HWP) which
is remotely controlled to within an uncertainty of 0.01°, enabling us to rotate the linear polarization of the light beam. To differentiate between the four NV orientations, we applied an external magnetic field.

Initially, we recorded the ODMR spectra of the \{111\} diamond for several polarization angles. The ground state spin-level population is correlated with the optical excitation probability; as it is increased, more population is optically pumped to $m_s = 0$ and can be transferred to $m_s \pm 1$ by the microwave radiation. Consequently, the contrast of the ODMR signal, on resonance, is proportional to the excitation probability of NV centers from the corresponding orientation. As shown in Fig. 3.10, the contrast of the ODMR resonances arising from NV orientations 2 – 4 changes with the polarization angle, while the dip representing the NV1 orientation is hardly influenced by it.

We have summarized these measurements by plotting the contrast at the transition peak of each NV orientation against the polarization angle. The results [Fig. 3.11(a)] correspond to the dependence predicted by Eq. (3.8)\(^2\). However, the curves are far from being smooth in these initial experiments, and it is hard to locate the exact angle for maximum excitation.

In subsequent experiments, we improved our experimental technique by using a lock-in amplifier to enhance the SNR. The technique is illustrated by the block diagram in Fig. 3.11(b). In this method we excite a single NV orientation each time (as before, we separate

\(^2\) Notice that in the experiment the contrast of NV1 is higher than the maximal contrast for any of the other orientations, although according to the theory they should be equal. This arises from the anisotropy of the fluorescence [82]. In the usual setup (the detector is on the same line as the objective and the diamond), fluorescence collected from the NV1 orientation is higher than for the other orientations. This issue is discussed later in this chapter.
**Figure 3.10:** The effect of polarization angle on the ODMR spectrum for a \{111\} diamond. Three different ODMR spectra for three different linear polarization angles of the exciting green light are shown. The NV1 label (in the inset) denotes the \{111\} orientation, wherein the light propagates along the N-V symmetry axis. The other three orientations, NV2, NV3, and NV4 make an angle of 109.5° with the light propagation vector. Note that each one of the four dips is split into three due to the interaction with the $^{14}$N nuclear spin [see Sec. (2.3.2) for more details].

the orientations using an external magnetic field) with a microwave resonant pulse, making the fluorescence blink at the pulse frequency. This is exhibited in Fig. 3.11(c). Since the other orientations are not influenced by the microwave pulse, their fluorescence level is constant over time. By mixing the fluorescence signal with the pulse frequency in the lock-in amplifier, we retrieve a signal which is proportional to the “blinking intensity”. We monitor this signal vs. the polarization angle.

As demonstrated in Fig. 3.11(d), the lock-in signal is less noisy than
the fluorescence signal and the angle of maximal excitation probability for a particular orientation can be extracted easily.

![Figure 3.11: Lock-in technique for selective polarization excitation. (a) The effect of the polarization rotation on the ODMR contrast (no lock-in is used). The different colors represent the different NV orientations (corresponding to the labeling in the text). The solid lines are to guide the eye. (b) A block diagram of the experimental system. The microwave frequency is set to the resonance of a particular NV orientation, and the microwave signal is pulse-modulated at 2.4 kHz. The modulation signal is simultaneously fed to the lock-in amplifier as a reference. The signal from the avalanche photodiode (APD) is fed to the input of the lock-in amplifier. We change the polarization angle using a motorized half-wave plate between lock-in output readings. (c) A qualitative illustration of the microwave pulsing influence on the APD signal. (d) The fluorescence contrast for the different NV orientations vs. the light polarization angle, as measured using the lock-in technique.](image)

If one wishes to excite just one orientation while suppressing the other three without the aid of an external magnetic field, Fig. 3.11 proves this to be impossible for the \{111\} configuration, mainly due to the NV1 orientation which, as shown in the graph, exhibits a constant and maximal signal. In addition, the 60° phase difference between the different excitation curves is not ideal. Naturally, only
a 90° difference ensures that while one orientation is at a maximum the other is at a minimum and vice versa. This happens only for the \{100\} configuration, as shown in Fig. 3.12.

![Figure 3.12: Experimental measurements of the contrast for resonances representing the various NV orientations vs. the green light polarization for a \{100\} diamond. The measurement was done using the lock-in technique. In this configuration the response to the polarization of two of the orientations is out-of-phase from the response of the other two. Note that the error bars here are high comparing to those obtained in Fig. 3.11(d) since the fluorescence level was generally much lower.](image)

Working with a \{100\} diamond, the angle between all the NV orientations and the \(k\)-vector of the green light is 54.75°, so Eq. (3.7) becomes

\[
I = I_0 \left( \sin^2 \phi_i + \frac{1}{3} \cos^2 \phi_i \right),
\]

with a minimal value of \((1/3)I_0\). Choosing an ideal polarization angle in the experiment (e.g. \(\phi = 50°\) in Fig. 3.12), it seems that up to 80% of the fluorescence may originate from two orientations and 20% will originate from the other two.

Unfortunately, the 80% proportion is equally divided between two orientations, and thus an addressing of just one orientation requires
the suppression of one of the two. To achieve this, one may take advantage of the fact that the red fluorescence of the NV center is anisotropic – the photons emitted are randomly polarized (at room temperature) in the $x_iy_i$-plane, and each photon can move only in a direction perpendicular to its polarization. Consequently, the best place for our detector to collect the maximum fluorescence from a given NV orientation would be with its plane perpendicular to the corresponding NV axis. In this position the light path to the detector is in principle allowed for all possible fluorescence polarizations. Following this logic, the worst place for placing the detector (in terms of collection efficiency), but the best place (in terms of orientation suppression), would be with its plane parallel to the NV axis. In this position, none of the photons that are polarized in the direction of the detector can move towards it. For illustration we have drawn a schematic diagram for these two scenarios (Fig. 3.13).

As the two NV orientations still unsuppressed by the green light polarization both have an angle of $109.5^\circ / 2$ from the $\hat{z}'$ axis (which is perpendicular to the diamond facet), positioning the detector so that it can completely suppress one of the remaining NV orientations means that the detector will receive photons that were emitted by the last NV at an angle of 54.75 degrees relative to the surface. However, due to the high index of refraction of diamond ($n \approx 2.4$), the path of the photons is strongly refracted, and they might even suffer total internal reflection from the diamond’s surface. Hence, emission from the remaining NV will also not make it to the detector. This makes the suppression of the fluorescence from a single orientation quite complicated. One of the options, which we are currently considering, is to use diamonds with an anti-reflection coating to minimize reflections from the diamond surface.
3.4 Summary: Properties of a magnetic sensor developed at Ben-Gurion University

In this section we describe the characterization of a diamond magnetic sensor called “Sumi” as conducted in our lab. The properties of this sensor are detailed in Table 3.2(a-b).

We measured ODMR spectra using the following experimental parameters [see Table 3.2(c)]: the waist and the power of the green laser were fixed at 3 mm (before the objective) and 30 mW respectively, while the microwave power was set to $-1 \text{ dbm}$ (before amplification).
In addition, the different NV orientations were separated using an external magnetic field.

The ODMR spectrum of Sumi is shown in Fig. 3.14. Using a Lorentzian fit to the spectrum (solid red line) we determined the linewidth ($\Delta \nu$) and the frequency of each resonance. The narrowest resonance line was then selected (in this case we have chosen the peak labelled 4 on the graph) to evaluate the ensemble coherence time, $T_2^*$, via [33]

$$T_2^* = \frac{1}{\pi \Delta \nu},$$

where we have assumed that the single-NV coherence time $T_2$, and the longitudinal spin coherence (thermal relaxation) time $T_1$, are several orders of magnitude longer than $T_2^*$ [61]. Note that in Sec. (3.1.2), we evaluated $T_2^*$ via the decay of the two-level Rabi oscillations measured with the Sumi diamond, and found it to be approximately five times longer than the value determined here ($T_2^* = 90$ ns). This difference originates in the measurement sequence: the process here is less coherent as we scan over the microwave frequency without pumping it back to the initial state [this can be partially compensated by increasing the laser power, as explained in Sec. (3.1)]. In the Rabi process we apply a single short microwave pulse after the system is pumped properly into the $m_s = 0$ level. For purposes of magnetic sensing, the value of $T_2^*$ extracted from the ODMR spectrum is naturally more appropriate, since this is the method used for the magnetic field measurement.

A lower bound to the shot-noise limit sensitivity (i.e. the best sensitivity achievable with this setup) is determined by assuming the largest detection volume possible, meaning the excitation light is focused exactly at the middle of the diamond plate and the fluorescence
Figure 3.14: An ODMR spectrum of the Sumi diamond. The experimental data was fit by a set of four Lorentzians. This diamond is cut along the \{111\} axis meaning the peaks labelled 1 and 4 belong to non-degenerate orientations, while 2 and 3 each represent triply-degenerate orientations. The center frequency and width of each Lorentzian are shown on the graph, as extracted from the fit.

is emitted from the volume of the two cones generated. The height of each cone is 250 \( \mu \text{m} \) which is half of the sample thickness, and their diameter is approximately 180 \( \mu \text{m} \). To find the number of probed NV’s we multiply this detection volume (i.e. the volume of the two cones) by the NV density. Note that we have converted the NV concentration given in ppm to density units using the formula: 1 ppm = \( 10^{-6} \cdot 6 \times 10^{23} [\text{mol}^{-1}] \cdot 3.5 [\text{g/cm}^3]/12 [\text{g/mol}] = 1.76 \times 10^{17} \text{ cm}^{-3} \) where \( 6 \times 10^{23} \) is the Avogadro constant, 3.5 [g/cm\(^3\)] is the density of the diamond, and 12 [g/mol] is the atomic weight of carbon.

Introducing the value of \( T_2^* \) as well as the number of the probed NV’s \( N \), the signal contrast and the detection efficiency \( \eta \) [all given
in Table 3.2(d) into Eq. (2.9), we find the lower bound on the shot-
noise limit of the sensor’s sensitivity.

Next, we used the corresponding lock-in signal [Fig. 3.15] to evaluate
the intrinsic sensitivity of the sensor. This is done by introducing to
Eq. (2.8) the measured slope of the signal \( \frac{dS}{dB} \approx \frac{Rg\mu B}{\Delta \nu} \), where \( R \) is the signal contrast and where we have converted \( \Delta \nu \) into magnetic
field units. In addition, we estimate \( \delta S \) to be the standard deviation
of our signal. The relevant numbers and the experimental sensitivity
calculated are given in Table 3.2(e).

Figure 3.15 shows the sensitivity calculation. In Fig. 3.15(a) the full
ODMR lock-in signal obtained with the Sumi diamond is shown. In
Fig. 3.15(b) we focus on one of the resonances [labelled as resonance
number 4 in Fig. 3.15(a)]. To calculate the signal slope \( \frac{dS}{dB} \) and
the standard deviation \( \delta S \), we fit the error signal near the resonance
to a Lorentzian derivative [Fig. 3.15(c)]. A similar line would be ob-
tained by a linear fit of the data near the resonance. In Fig. 3.15(d),
which is an additional zoom-in of the error signal, we illustrate the
sensitivity calculation: the values for the contrast and the frequency
width are indicated on the graph. The standard deviation of the
signal is estimated as the root mean square (RMS) error of the fit
and denoted \( \delta S_{\text{rms}} \).

The shot-noise limited sensitivity of the sensor is much better (by \( \sim \)
4 orders of magnitude) than the actual sensitivity measured. One
reason may be that the actual detection volume is much smaller. In
addition, one may suspect that the actual sensitivity is governed by
the various sources of noise in the experiment, rather than by the
physical parameters of the sensor.
The shot-noise limit (calculated with the $T_2^*$ extracted from the data) already accounts for both homogeneous and inhomogeneous line broadening (coming from strain, interaction with the spin of the $^{14}$N electrons and with the spin of the $^{13}$C nucleus), so the noise may be attributed to transient systematic errors such as temperature fluctuations, external variations in the magnetic field, and technical noise.
For example, light shot noise may contribute to the overall fluctuations. However, in our case, the detector receives about 1 mW or about $10^{16}$ photons per second, meaning that the shot noise is at the $10^{-8}$ level, much lower than the noise we observe.

Another source may be temperature fluctuations. As mentioned in Sec. (3.2), temperature fluctuations on the order of 1 mK induce a magnetic uncertainty of $\sim 3 \text{nT}$. As the pulsed microwave radiation heats the diamond, and since we do not stabilize the temperature in any way, we expect the magnetic noise to exceed this value.

External variations in the magnetic field of 1 mG and above are quite common in an unshielded environment, which is the kind of environment we are working in. Note that this noise is only one order of magnitude lower than the sensitivity measured, so it is probably the main source of noise in the system.
a. The properties of the diamond plate

<table>
<thead>
<tr>
<th>Diamond</th>
<th>Production process</th>
<th>Size [mm]</th>
<th>Orientation</th>
<th>[N] [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sumi</td>
<td>HPHT</td>
<td>3 × 3 × 0.5</td>
<td>{111}</td>
<td>≤ 100</td>
</tr>
</tbody>
</table>

b. NV generation process

<table>
<thead>
<tr>
<th>Diamond</th>
<th>Irradiation energy [MeV]</th>
<th>Dose [cm$^{-2}$]</th>
<th>[NV$^-$] [ppm]</th>
<th>NV density [cm$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sumi</td>
<td>~ 3</td>
<td>1 × 10$^{18}$</td>
<td>16</td>
<td>2.8 × 10$^{18}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Annealing temperature [°C]</th>
<th>Annealing time [hours]</th>
</tr>
</thead>
<tbody>
<tr>
<td>850</td>
<td>3.5</td>
</tr>
</tbody>
</table>

c. Probing conditions

<table>
<thead>
<tr>
<th>Diamond</th>
<th>Detection volume [cm$^3$]</th>
<th>Laser power [mW]</th>
<th>Microwave power [dBm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sumi</td>
<td>2.2 × 10$^{-6}$</td>
<td>30</td>
<td>-1</td>
</tr>
</tbody>
</table>

d. ODMR signal properties

<table>
<thead>
<tr>
<th>Diamond</th>
<th>Contrast</th>
<th>$\Delta\nu$ [MHz]</th>
<th>$\eta$</th>
<th>$N$ [10$^{12}$]</th>
<th>$T_2^*$ [ns]</th>
<th>Shot-noise limit [T/$\sqrt{\text{Hz}}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sumi</td>
<td>0.025</td>
<td>3.5</td>
<td>0.01</td>
<td>7 × 10$^{12}$</td>
<td>90</td>
<td>~ 0.92 × 10$^{-10}$</td>
</tr>
</tbody>
</table>

e. Error signal properties

<table>
<thead>
<tr>
<th>Diamond</th>
<th>Contrast</th>
<th>$\delta S_{\text{rms}}$ [V]</th>
<th>Exp. sensitivity [T/$\sqrt{\text{Hz}}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sumi</td>
<td>1.1</td>
<td>0.01</td>
<td>$1 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

The numbers here were extracted for one second integration within a window of ~ 0.4 MHz. Each window consists of an average of 100 measurements taking 10 ms each.

Table 3.2: Tables summarizing the process of the diamond sensor preparation and optimization. (a) This table exhibits the properties of the diamond plate including the production process, the size, the orientation and the initial nitrogen concentration. (b) This table shows the NV generation process consisting of irradiation and annealing in an inert atmosphere. (c) In this table we have inserted the experimental parameters, namely the detection volume, the laser power and the microwave power. (d-e) Here we show the parameters of the ODMR and error signals obtained in the experiment. From the ODMR parameters we calculate the shot-noise limit [using Eq.(2.9)]. Note that the collection efficiency $\eta$ is evaluated experimentally in our system. The contrast and the linewidth $\Delta\nu$ are extracted directly from the signal [Fig. 3.14]. The number of NV centers $N$ is estimated using the detection volume and the NV concentration. The ensemble coherence time $T_2^*$ is calculated from the linewidth using Eq. (3.10). The experimental sensitivity is calculated from the error signal parameters (contrast and width) as they appear in Fig. 3.15(d).
Chapter 4

Diamond magnetometry of a thin film superconductor

4.1 Background and motivation

The study of magnetic phenomena in superconductors and the search for superconductors possessing high critical temperatures ($T_c$) [83–85] require adequate measurement techniques. Direct signatures of superconductivity (diamagnetism and vanishing resistivity) may be complemented by measurements of one or more properties such as local density of states, nuclear magnetism, or heat capacity. Of particular interest is the study of magnetic vortices in type-II superconductors, which is the focus of this work. Type-II superconductors exhibit phase transitions at two critical magnetic field values, with the lower denoted $H_{c1}$ and the higher, $H_{c2}$. For magnetic fields $H < H_{c1}$, these superconductors exhibit the Meissner effect, whereby magnetic flux is expelled from the interior. In the mixed state, $H_{c1} < H < H_{c2}$, magnetic flux can penetrate through the cores of superconducting vortices. Each vortex, which carries a single quantum of magnetic flux, consists of a core, where superconductivity is suppressed within
a radius $\sim \xi$ (the coherence length), surrounded by circulating supercurrents, which persist over a length scale $\sim \lambda$ (the penetration depth)$^1$. The coherence length and the penetration depth are depicted in Fig. 4.1.

![Figure 4.1: An illustration of the two characteristic lengths of a superconducting vortex. The red curve exhibits the current density of the circulating supercurrents, while the blue curve describes the magnetic field generated by these currents. Both curves are qualitative and with respect to the distance $r$ from the center of the vortex. The coherence length and the penetration depth of the superconductor are denoted by $\xi$ and $\lambda$, respectively.](image)

The structure and magnetic properties of vortices are of interest in the study of pnictides, which feature irregular arrays of vortices [86], and in the search for multi-component superconductors that are predicted to contain vortices with fractional multiples of the flux quantum [87, 88]. The motion of vortices is also of interest, because it leads to energy loss that degrades the performance of almost all superconducting devices. Vortex motion also determines the critical current density of superconductors, see for example Ref. [89], and can serve as a model for condensed-matter flow [90]. Reduction of

---

$^1$ This description of critical field is general and doesn’t account for geometrical factors which are treated in Sec. 4.1.1 below.
vortex motion has been achieved through the use and engineering of pinning centers [91, 92].

The physics of pinning centers has been explored mainly through macroscopic measurements of properties such as electrotransport and bulk magnetization. These integrated-response techniques conceal the details of the microscopic properties of vortex pinning. Thus, efforts have been devoted toward developing real-space imaging methods for direct visualization of vortex patterns. Magnetic imaging enables obtaining accurate values of the penetration depth, which reports on the number density of electrons involved in superconductivity, the nature of the superconducting state [93] and the types of vortex interactions which can occur [94]. Aside from capturing vortex structure, techniques that feature video frame rate may enable studies of vortex dynamics [92, 95].

Several methods have been investigated for vortex visualization [96] such as magnetic-resonance force microscopy (MRFM) [97], scanning magnetic probes [98–100] (including scanning Hall-probe microscopy [101]), Lorentz microscopy [102], magneto-optical imaging systems (polarized-light microscopy) [103, 104], and transmission electron microscopy (TEM) [105]. High spatial (better than 20 nm) and temporal resolution is offered by the TEM. A tilted sample features vortices that penetrate normal to the surface of the film to provide a component of the B-field normal to the electron beam, causing the electrons to be deflected by the Lorentz force and appear as black-white features in an out-of-focus image [102, 105, 106]. However, TEM has been limited, so far, to low external fields (< 30 G) [105], whereas many type-II superconductors such as Nb₃Sn and
NbTi possess upper critical fields that are much higher. Furthermore, the destructive nature of the measurement, which causes rapid damage to the sample, prohibits studies over long periods of time.

The MRFM method can achieve spatial resolution which is similar to that of TEM [107]. However, this measurement technique perturbs the magnetism of the sample to be measured, as it is based on getting the sample’s magnetization to oscillate at the cantilever frequency. In addition, the MRFM sensitivity is severely compromised at higher sample temperatures making it a less-than-ideal technique for the imaging of high Tc superconductors.

The quest for non-destructive and non-perturbative methods has led to the development of magneto-optical imaging systems. These systems take advantage of magneto-optical materials that change the polarization of light in proportion to the surface magnetic field. In recent years this technique has become a leading method in vortex imaging, giving rise to sub-micron spatial resolution and a $\sim 10 \mu T$ magnetic field resolution [108–110]. Nevertheless, the imaging of a single vortex remains a challenge for this technique, as it is hard to keep a sub-micron gap, necessary for this kind of imaging, between the magneto-optical layer and the superconducting sample. In addition, the sensitivity reported to date ($\sim 10 \mu T$) may be insufficient for accurate measurements of the vortex properties.

Magnetometry with NV centers in diamond is a good candidate technique for non-destructive sensing with high spatial and temporal resolution over a wide range of external magnetic fields. High spatial resolution can be achieved in a scanning-probe configuration [37, 111, 112] or through the use of sub-diffraction imaging methods, such as stimulated emission depletion (STED) and ground-state
depletion (GSD), where resolutions down to several nanometers are possible [113]. Such a spatial resolution may allow visualization of the vortex core or imaging individual superconducting nano clusters. The sensitivity of NV centers in diamond, which was investigated at the single NV center level [11, 12, 37] and for ensembles [13, 14], is such that NV-diamond sensors are capable of detecting electron spins [114] and nuclear spins [115] located external to the diamond. Finally, by depositing or growing the superconductor film directly on the diamond or by attaching two highly polished surfaces, it is expected that the sensor-sample gap would be in the nanometer range.

In a previous study, detection of the Meissner effect in a type-II superconductor with NV centers was demonstrated [39] by sensing the fringe field of a macroscopic sample. The approach investigated in the present work is to generate a 10 nm thin layer of NV centers within \( \approx 25 \) nm of the surface of the diamond and to detect the shift of their magnetic resonance using a focused laser beam. The beam waist is approximately 1 \( \mu \)m in diameter, leading to detection volumes on the order of \( 10^{-20} \) m\(^3\). A thin layer with a small sensor-sample gap enables high spatial resolution.

Recently, vortices in permalloy thin films were imaged using a single NV center [116–118]. We choose instead to use an ensemble of NV centers, which will ultimately enable us to image the magnetic field in a larger area in a single shot (i.e. no scanning) and with a higher sensitivity (\( \delta B \propto 1/\sqrt{N} \)). In addition, with an ensemble we can measure all three components of the magnetic-field vector simultaneously.

In this study we utilize an NV sensor to characterize a thin layer (300 nm) of type-II superconducting yttrium barium copper oxide
(YBCO) material. Using this sensor, we observe the Meissner effect and characterize the superconducting phase transition. We also demonstrate the ability to monitor the penetration field of vortices, locally. Finally, as an outlook, we describe a new superconducting device containing a micro-patterned superconducting layer which is designed to test the resolution of the sensor and its ability to map single vortices. We discuss the implications for imaging individual vortices or arrays of vortices.

4.1.1 Special properties of a thin film superconductor

The reaction of a superconductor to the presence of an external magnetic field depends strongly on the sample geometry and on the field direction [119]. For an infinite cylindrical conductor subjected to a parallel magnetic field the vortices uniformly fill the entire surface at the critical field $H_{c1}$. However, for differently shaped superconductors, the penetration of vortices may be anisotropic.

In particular, we are interested in this study in the case of a thin film subjected to an external field perpendicular to the surface. In the Meissner state, wherein the magnetic field is fully expelled by the film, the field lines are “bent” and concentrated mostly at the edges of the film, leading to the formation of vortices at the edges at field intensities much lower than $H_{c1}$. This behaviour is illustrated in Fig. 4.2(a). As we increase the field, the distribution of vortices expands towards the center of the film leaving a “vortex-free” zone denoted in the figure by $a$. For comparison, we show the long cylindrical conductor case in Fig. 4.2(b) where the surface perpendicular to the external field is small in comparison to the thickness of the
sample. Here the vortices uniformly fill the whole sample at $H_{c1}$, as shown by the schematic figure.

For a film with a thickness $d$ much smaller than its width $w$, the “vortex-free” width (in the presence of an applied perpendicular field $H_0$) is given by [120]

$$a = \frac{w}{\cosh \left( \frac{H_0}{H_f} \right)},$$  \hfill (4.1)

where $H_f = (4/c) d J_c$ is the characteristic field for the film geometry (when a significant part of the surface experiences vortices), with $J_c$ and $c$ being the critical current density and the speed of light, respectively. In our experiments, described below, we apply an external field $H_0$ and measure the magnetic induction $B$, which is proportional to the number of vortices. The probing area (=the waist of our laser beam) is several microns while the sample size is $5 \times 5$ mm. Thus, in the regime $H_0 < H_f$, the measured field depends strongly on our sensor’s exact location above the sample as vortices do not occupy the full area. We further discuss this aspect in the experimental results section.

It is worth mentioning that there is an exception to the mechanism described above. In a film wherein there is no pinning of vortices, the expansion of their penetration is controlled by geometrical barriers [121]. As a result, vortices start penetrating from the center and not from the edges. Since a strong pinning force was observed in our sample, we will not expand further on this exceptional behavior.
**Figure 4.2:** An illustration of the effect of geometry on the external field lines and vortex penetration. (a) A thin film with a thickness \(d\) in a perpendicular field \(H_0\). The image on the top illustrates the compression of field lines at the edges leading to an early vortex penetration there. Below, a top view of the film is shown where the width of the sample and the “vortex-free” width are \(w\) and \(a\), respectively. (b) A long cylinder in a parallel field. The field lines in this case are hardly perturbed, and hence the vortices exhibit an homogeneous distribution across the sample surface at \(H_0 = H_{c1}\), as shown in the graph.

### 4.2 Superconducting thin film characterization with a diamond magnetometer

#### 4.2.1 Experimental technique

The experimental setup is shown in Fig. 4.3. Confocal microscopy is performed by excitation with green light (532 nm) supplied by a diode pumped solid-state laser. The output beam is expanded to a diameter of \(\sim 1\) cm, larger than the diameter of the objective
lens. This enables us to scan the beam across the sample, by moving the objective, without affecting the beam direction. The objective (Olympus, Pro Plan) has a numerical aperture N.A.=0.65 and a maximal working distance of f=4 mm. The laser light power at the sample location was measured to be 10 mW.

The fluorescence emitted by the NV centers is collected with the same objective used to focus the incident green light, and is transmitted through two dichroic mirrors, both mounted in cubes to facilitate optical alignment. These cubes are mounted on a 3D translation stage which is controlled by actuators. A lens is used to focus the fluorescence on a high-sensitivity photodiode (NewFocus 2151). To achieve higher spatial resolution we may use a \( \sim 5 \mu m \) pinhole to ensure that only fluorescence from the focal plane is collected.\(^2\)

The superconductor sample is mounted on the copper cold finger of a cryostat (Janis model ST-500) using a vacuum compatible varnish (VGE 7031 of LakeShore). To promote good thermal contact, we use a Teflon piece [not shown in Fig. 4.3] which is held by screws and presses the superconductor sample against the cold finger. We use a YBCO superconductor layer (obtained from Theva) with a thickness of 300 nm, which was deposited on a MgO substrate (5 \( \times \) 5 \( \times \) 0.5 mm\(^3\)). The \( c \)-axis of the superconductor is perpendicular to the plane of the film, so that the CuO\(_2\) planes are parallel to the surface.

Transmission of the microwaves to the diamond is achieved with two

\(^2\) The pinhole size is calculated in the following way: the fluorescence collected from the focal plane is collimated by the objective and focused on a photodiode using a lens (see Fig. 4.3). Assuming a Gaussian beam profile, the similar triangles relation \( z_R = \frac{2w_0}{\sqrt{2}} \approx f/(d/2) \) holds, where \( d \) is the fluorescence beam diameter, \( f \) is the focal length of the lens (see Fig. 4.3), \( w_0 \) is the waist at the focal point, and \( z_R = \pi w_0^2/\lambda \) is the Rayleigh range [122]. Introducing the relevant numbers for the fluorescence collected in our setup [\( d = 10 \text{ mm} \) (=the objective aperture), \( f = 30 \text{ mm} \) and \( \lambda = 700 \text{ nm} \)], we find that the diameter of the fluorescence beam coming from the focal plane and focused on our photodiode is \( 2w_0 \approx 3.6 \mu \text{m} \). Hence a pinhole of 5 \( \mu \text{m} \) is a reasonable choice for our setup.
copper strips placed along either side of the diamond on top of the superconducting layer [see Fig. 4.3].

To ensure we measure only the magnetic fields associated with the superconductor layer, compensation coils are employed. These coils enable the zeroing of the Earth’s magnetic field and stray static fields from other sources.

The sensor used in this work is a diamond plate which contains a layer of NV centers near the surface. Since the field in the center of a magnetic vortex decays at short distances approximately as $B_0 e^{-z/\lambda}$ ($B_0$ being the field at the surface, $z$ the distance from the surface, and $\lambda$ the field penetration depth; for YBCO $\lambda \approx 150$ nm$^3$, there is a gradient of the field across the sensor that leads to line broadening [123]. Thus a thin sensor layer is required to minimize broadening and thereby increasing sensitivity. An optimal thickness must be found as too thin a layer reduces sensitivity due to the small number of NV centers. In any case, the thickness cannot be higher than the required spatial resolution for the same reason that the NV layer needs to be close to the diamond surface and consequently to the sample.

To meet these requirements, a diamond with a thickness of 80 $\mu$m produced by Element Six was implanted with N$^+$ ions at Core Technologies. The ion beam energy and the irradiation dose were 10 keV and $10^{13}$ cm$^{-2}$, respectively. Monte-Carlo simulations using the software of Ref. [124] indicate that the resulting layer of the implanted nitrogen atoms is located between $z \approx 15$ nm and $z \approx 25$ nm, where $z = 0$ is at the diamond surface. To generate NV centers, the diamond was annealed in an inert atmosphere (Ar) at 800$^\circ$C.

$^3$ A longer and more accurate expression for the field is given in Sec. (4.3.1)
Following Ref. [125], we also annealed the diamond in an oxygen atmosphere (60/40% of Ar/O\textsubscript{2}) at 400°C to enhance conversion of neutrally charged centers (NV\textsuperscript{0}) into negatively charged ones (NV\textsuperscript{−}). The NV\textsuperscript{−} centers are used for magnetometry, whereas the NV\textsuperscript{0} centers produce undesirable background fluorescence. The effect of the
extra annealing is seen in Fig. 4.4(a) as a much higher signal contrast of the annealed sample. We estimate that one to five percent [126] of the implanted ions formed NV\(^-\) centers, and therefore the density of NV\(^-\) centers is \(\sim 1 - 5 \times 10^{11} \text{ cm}^{-2}\). Focusing the laser beam to a size of 1 \(\mu\text{m}^2\) should yield \(\sim 1,000 - 5,000\) NV\(^-\) defects within the sensing volume.

The diamond surface is polished along a \{110\} plane, meaning that two of the four possible alignments of the NV axes are at \(\cos^{-1}(\sqrt{2}/3) \approx 35^\circ\) with respect to the normal to the crystal plane (the out-of-plane axes) and the other two are at \(90^\circ\) (in-plane axes). The extraction of the magnetic field from the \{110\} spectrum is detailed in Sec. (2.4.1).

The intrinsic sensitivity of the sensor depends mainly on the diamond characteristics. Using a lock-in amplifier, we can suppress noise from external sources and improve the signal-to-noise ratio, as shown in Fig. 4.4(b). The lock-in technique used here involves frequency modulating the scanning microwaves with a modulation depth of 6 MHz and a frequency of 500 Hz (this signal also serves as the lock-in amplifier reference). Measuring the sensitivity in the same manner described in Sec. (3.4), we find \(\delta B \approx 2 \mu\text{T}/\sqrt{\text{Hz}}\). While this sensitivity may be further improved through optimization of the diamond sensor, it does satisfy the demands of the current experiment.

### 4.2.2 Experimental results

After cooling to \(\sim 60\) K, the sample is heated in steps of 1 K while recording the ODMR spectra at each step. During these measurements, an external field of \(\sim 15\) G is applied along \(\hat{z}\), which would
Figure 4.4: Signal enhancement of the diamond sensor. (a) A comparison of ODMR spectra obtained before (blue line) and after (red line) sample annealing in oxygen. The contrast is enhanced due to conversion of NV\(^0\) centers to NV\(^-\). (b) An error signal (blue line) derived from the fluorescence signal (green line). The signal-to-noise ratio (SNR) is greatly enhanced.

ordinarily produce an ODMR splitting of \(\sim 69\) MHz \([= 15 \times 2 \times 2 \times 1.4 \times \cos(35^\circ)]\) in the absence of a superconducting sample, where \(\mu_B = 1.4\) MHz/G is the Bohr magneton, and where we have approximated the Landé factor \(g_s\) by 2. However, none of the ODMR spectra below \(T_c\) showed any Zeeman splitting due to this field [see
Fig. 4.5(a)]. A small splitting of 13 MHz is observed, but this splitting is also observed in the absence of external fields and can be attributed to an intrinsic non-axial strain field within the sensor [127]. At $T=70$ K, Fig. 4.5(b), we observe a larger splitting, 42 MHz, which is still less than the expected Zeeman splitting in the absence of the superconductor. This indicates the onset of the superconducting phase transition. At $T=74$ K [see Fig. 4.5(c)] we finally measure a splitting in the ODMR signal which corresponds to the external field. We then reduced the temperature below $T_c$, namely to $T=67$ K [see Fig. 4.5(d)] and found that the Zeeman splitting remains largely unchanged from the value above $T_c$. The hysteresis can be attributed to the vortices created as we have entered the mixed state of the superconductor (for H-T diagrams of superconductors see Ref. [119]). Upon reducing the temperature further to $T=60$ K, we turned off the applied field, Fig. 4.5(e). Strikingly, the ODMR spectrum retains the splitting observed for $T > T_c$ when the field was applied. This is the signature of flux trapping, whereby vortices remained pinned to defects in the superconductor even in the absence of an applied field. Figure 4.5(f) summarizes the sequence described above, and presents the Zeeman splitting variation as a function of temperature for both ascending and descending sequences.

Since the signal obtained with the lock-in amplifier is the derivative of the ODMR spectrum, we have analyzed the signal at each temperature by fitting a sum of $N$ Lorentzian derivatives ($N$ being the number of resonances in the spectrum),

$$F(\omega) = \sum_{i=1}^{N} A_i \frac{-2\gamma_i(\omega - \omega_i)}{[(\omega - \omega_i)^2 + \gamma_i^2]^2},$$

(4.2)

where $\gamma_i$ is the linewidth of the $i$-th resonance and $\omega_i$ is its center, or
the zero crossing of the error signal. $A_i$ are the resonance amplitudes. As a measure of the magnetic field, we use the frequency separation between the magnetic resonances, $0 \rightarrow 1$ and $0 \rightarrow -1$, of the $35^\circ$ orientations. The error in determining this separation is calculated from the fit.

The accuracy of the fitting depends on the phase of the lock-in signal. We have adjusted this phase to be a multiple of $\pi/2$, meaning that on one channel the error signal is maximized whereas on the other channel the original ODMR signal is observed. This method yields reliable zero crossing values when fitting.

Fitting the blue dots of the experimental data to a sigmoid function [39]

$$\Delta Z(T) = \frac{a}{1 + \exp[-(T - T_c)/\Delta T_c]} + b, \quad (4.3)$$

where $a$, $b$, $T_c$ and $\Delta T_c$ are fitting parameters, we find that the critical temperature of the thin film layer and the width of the phase transition are $T_c = 70.0(2)$ K and $\Delta T_c = 0.5(1)$ K, respectively.

Next, we monitored the sample’s response to an external perpendicular magnetic field while the field was increased from zero.

From the discussion regarding the gradual formation of vortices across the surface in the thin film geometry appearing in Sec. 4.1.1 we conclude that exactly in the center of the superconducting square, a high external field is required in order to observe vortices (according to Eq. (4.1), for $a \rightarrow 0$ we need $H_0 \gg H_f$), while at the edges they appear at rather low fields. Since we cannot know the exact place of our probe in the current setup, it is hard for us to experimentally map the penetration field across the layer (this issue is solved by a wide field imaging setup which is now being built in our lab). We
Figure 4.5: (a–e) Several ODMR signals taken at different temperatures with an applied external magnetic field of 15 G. The dashed black lines denote the Zeeman splitting for each case. The up/down arrows indicate raising or lowering of the temperature. (a) An ODMR signal taken below $T_c$, at 62 K. The system is in the Meissner state, and the external field does not penetrate the superconductor layer. (b) The signal at the phase transition. Here we see a partial penetration of the field (a Zeeman splitting of 42 MHz corresponds to a field of $\sim 9$ G in the $\hat{z}$ direction). (c) This signal, at 74 K, indicates that the system is no longer in the superconducting phase. In this graph we also demonstrate the fit to a derivative of a Lorentzian function, used to determine zero crossings of the error signal. We use this fit on all ODMR signals to find the value of the Zeeman splitting. (d) Signal at 67 K, namely after taking the temperature down again, without turning the external field off. Since the critical field at $T_c$ is zero, vortices penetrate the layer, leading to the average magnetic field that we measure. (e) As detailed in the text, at 60 K the magnetic field was turned off. Defects in the superconductor layer lead to flux pinning, evidenced by the field measured by the NV centers. (f) The phase-transition curve of the superconductor layer. Plotted is the Zeeman splitting between the 0 → 1 and the 0 → −1 resonances of the 35° NV-axis alignments. The blue data points belong to the ascending temperature sequence, while the red ones belong to the descending sequence. The external field during the measurements was $\sim 15$ G except for the last measurement (at $T = 60$ K), where the field was turned off. We fit the blue data points to a sigmoid function (blue line), and extract a critical temperature of $T_c = 70.0 \pm 0.2$ K. The red line is to guide the eye.
did, however, see that when we measure at the edge of the layer we observe vortex penetration at low field (several Gauss), and when we measure at the middle we get to the maximal field our coil can provide (∼100 G) without observing vortex penetration. Finally, we chose to put the probe at a point which is approximately midway between an edge and the center, so the change in the local magnetization (or the measured magnetic field) due to the penetration of vortices may be observed.

Gluing the diamond on the sample with a cryogenically compatible varnish, as was done here, resulted in a distance between the surfaces of the diamond and the sample which is >10 µm (measured using a digital gauge). At such a height above the sample, the field measured is the averaged local field of the vortices, namely, $B = \phi_0 n$, where $\phi_0 = 20.7$ G·µm$^2$ is the flux quantum [119], and $n$ is the number of vortices per unit area. As mentioned above, in the future we intend to use the setup for imaging vortices. For such a measurement the distance between the detector and the superconductor sample must be kept smaller than ∼1 µm [128]. Such proximity is enabled only by depositing or growing the superconductor on the diamond or by special bonding techniques which we are now exploring (e.g., welding of gold nanodots deposited on both surfaces).

In the present experiment, we increase the current in the coil, starting from zero and in increments of 1 A (corresponding to ∼4.5 G), and record the ODMR spectrum each time. After we cross the penetration field $H_P$ (the magnitude of the applied external field resulting in the onset of vortex formation), we gradually decrease the current to zero. The temperature is kept at 65 K for the entire sequence.
The results of these measurements are presented in Fig. 4.6. In Fig. 4.6(a) we see that below $H_P$, the Zeeman splitting is relatively small, indicating the absence of vortices. At $I_{coil} \approx 10$ A, we observe a sudden increase of the measured Zeeman splitting due to the formation of vortices. Next, the field is gradually eliminated, but a substantial Zeeman splitting of $\sim 103$ MHz is still measured between the two magnetic resonances of the NV centers with 35° axes [see Fig. 4.6(b)]. In the absence of a superconductor, a field of $\sim 22.5$ G would normally be required to produce such a splitting. The reason for this hysteresis is pinning of vortices by defects in the lattice: upon crossing the critical field, vortices are generated and trapped by microscopic defects within the sample [119]. As we lower the field, the vortices remain trapped because the pinning force is field-independent. In this regime we measure the field of trapped vortices.

Figure 4.6(c) summarizes the measurement sequence. The blue data points were recorded while increasing the current, and the red ones while decreasing it.

We may estimate the penetration field, $H_P$, using the data of Fig. 4.6(c). The sharp increase in the Zeeman splitting around $I_{coil}=10$ A is interpreted as the formation of vortices at the position of the sensor, which leads to a non-zero magnetic induction $B$ inside the material. The magnetic field corresponding to $I_{coil} = 10$ A is found by measuring the Zeeman splitting induced by this current above $T_c$, wherein the external field is no longer screened. Converting to units of magnetic field we find $H_P = 46.2 \pm 3.9$ G.

As reflected by the red data points in Fig. 4.6(c), the magnetic induction $B$ is almost completely preserved due to flux pinning when
the external field is decreased. This trapped flux corresponds to a magnetic field of \( B = 22.4 \pm 0.5 \text{ G} \). Note that \( B < H_P \) at this stage, indicating the external field does not fully penetrate the layer.

![Figure 4.6: (a-b) ODMR spectra taken during the experimental sequence for finding the local penetration field \( H_P \). The two different signals, taken with the same external field, reflect different responses of the material: (a) Taken after increasing the field from zero, meaning the system near the sensor is in the Meissner state, and the external field is screened. (b) Recorded after lowering the field from \( \sim 50 \text{ G} \), which is above \( H_P \), thus measuring the field of the pinned vortices. (c) The Zeeman splitting detected with the NV-diamond sensor during the measurement sequence. The applied magnetic field is proportional to the coil current. The plot demonstrates the local transition from the Meissner state to an intermediate state wherein vortices are in the sample. The blue points correspond to increasing coil current while the red points correspond to decreasing the current in the sequence, showing once again vortex pinning. The blue and red lines are to guide the eye.](image)

In addition, we performed an experiment where we cooled the system, in a weak field of \( \sim 10 \text{ G} \), down to 40 K. The resulting trapped flux corresponded to a magnetic field of \( 9.5 \pm 0.2 \text{ G} \), as calculated from the measured Zeeman splitting. This field corresponds to a vortex density of \( n = B/\phi_0 \approx 0.45 \pm 0.01 \mu\text{m}^{-2} \). Cooling the system with an applied field gives rise to vortices with a uniform density across the sample. Under these conditions, and by positioning the
sensor less than 1 µm above the surface, it should be possible to image an isolated vortex. Let us also note that as our resolution increases, namely, as our pixel size and therefore our detection volume is decreased, the sensitivity will only be suppressed inversely with the square root of the volume. In case we need to recover sensitivity, the thickness of the NV layer may be increased (e.g. by an order of magnitude), and in addition, the density of NV centers may be enlarged.

Finally, the properties of the superconductor measured in this work are listed in Table 4.1 below.

<table>
<thead>
<tr>
<th>Property</th>
<th>Measurement</th>
<th>Ref. Value</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_c$</td>
<td>70.0 ± 0.2 K</td>
<td>82.2 ± 0.3 K</td>
<td>Ref. value measured after sample growth</td>
</tr>
<tr>
<td>$\Delta T_c$</td>
<td>0.5 ± 0.1 K</td>
<td>0.14 ± 0.01 K</td>
<td>same as above</td>
</tr>
<tr>
<td>$H_p$</td>
<td>46.2 ± 3.9 G</td>
<td>None</td>
<td>local measurement</td>
</tr>
<tr>
<td>$n$</td>
<td>0.45 ± 0.01 µm$^{-2}$</td>
<td>None</td>
<td></td>
</tr>
</tbody>
</table>

**Table 4.1:** Superconductor-layer properties measured by the NV sensor. The reference values were also measured in our lab. We have used a miniature coil located on one side of the sample to transmit an AC signal of a $\sim 1$ kHz frequency. A pickup coil, identical in specifications to the transmitting coil, is placed on the other side of the sample. The whole structure is shielded with copper rods and dipped in liquid nitrogen. The shielding decreases the rate of sample cooling, enabling us to monitor the pickup coil signal vs. the temperature, in order to obtain the phase transition curve.

The significant drop between the reference transition temperature $T_c$ and the temperature measured in the experiment may be due to several reasons, among which are: (a) aging of the sample, (b) imperfect thermal contact between the YBCO chip and the cold finger where the temperature sensor is housed, and (c) heating of the YBCO by the green laser used for optically pumping the diamond and by the microwave radiation.
4.3 Towards on-chip vortex imaging

Magnetic field imaging of superconducting vortices requires some modifications to the experimental system we have used so far. First, a high-resolution imaging system, either a scanning probe microscope or a wide-field imaging setup, should be installed.

In a scanning probe configuration [see Fig. 4.7(a)], a confocal microscope is constructed to limit the volume from which fluorescence is collected. While limiting the collection in the $\hat{z}$ direction (perpendicular to the diamond’s surface) helps reduce background noise, the $xy$ resolution is crucial to the vortex imaging feasibility. To obtain diffraction-limited resolution, the size of the pinhole placed in front of the detector must be on the order of an Airy unit (AU) [129]. In our case that means using a $\sim 1 \, \mu m$ pinhole. Obviously, such a small aperture requires high accuracy in the optical alignment, as well as an ultra-sensitive detector. In addition, such a system would be highly sensitive to microscopic vibrations, and the scanning time over a surface is much too long to enable the recording of vortex dynamics.

We have therefore chosen to implement a wide-field imaging setup in our experiment. As shown in Fig. 4.7(b) we use a collimated green light beam rather than a focused one. To achieve maximum resolution, we adjust the system magnification according to the pixel size of our charged coupled device (CCD) sensor. For example, a magnification of $\times 20$ and a typical pixel size of $6 \, \mu m$ give an effective pixel size of $300 \, \text{nm}$ which is small enough considering the diffraction limit in our case (estimated as $\sim 500 \, \text{nm}$). A sensor with $1000 \, \times$
1000 pixels then dictates a maximum beam size of 300 µm, so that a relatively large area is imaged simultaneously in this configuration.

**Figure 4.7:** Two different configurations for optical imaging. (a) Scanning probe configuration. The green light is focused on the diamond by an objective, and the fluorescence is focused on the detector by an additional lens. The dotted red line denotes fluorescence that does not originate in the focal plane or focal spot of the objective, and is therefore blocked by the pinhole at the focal point of the second lens. (b) Wide-field imaging configuration. Here the green light is collimated and must be adjusted so that its focal point overlaps the focal point of the objective. The magnification of the system is given by \( \text{mag} = \frac{f_{\text{lens}}}{f_{\text{obj}}} \) and in order not to lose resolution must be adjusted so that the effective pixel size satisfies \( s_{\text{eff}} = \frac{s_{\text{real}}}{\text{mag}} \leq r_d \), where \( s_{\text{real}} \) is the real pixel size and \( r_d \) is the diffraction limit.

### 4.3.1 Vortex imaging simulations

As mentioned above, the magnetic induction \( B \) and the vortex density \( n \) are related via \( B = n\phi_0 \), where \( \phi_0 = 20.7 \text{G} \mu\text{m}^2 \). Hence, cooling the sample with an external field of 5 G results in trapping vortices with a density \( n \approx 0.25 \mu\text{m}^{-2} \), corresponding to a vortex
separation of \( \sim 2 \mu m \). These conditions, combined with an optical resolution on the order of the relevant diffraction limit, \( r_d \approx 500 \) nm, enable the magnetic imaging of a single vortex in our system.

The magnetic field induced by a single vortex at a height \( z \) and a distance \( r \) from its center is given by [123]

\[
B_z = \frac{\phi_0}{2\pi} \frac{z + \lambda_{\text{eff}}}{\left( r^2 + (z + \lambda_{\text{eff}})^2 \right)^{3/2}},
\]

where \( \lambda_{\text{eff}} = \coth \left( \frac{d}{2\lambda} \right) \) is the effective penetration depth with \( d \) being the film thickness. Using this equation, we have simulated the vortex field distribution at different heights above the surface. Figures 4.8(a) and 4.8(b) show the field distributions at \( z = 0 \) and \( z = 1 \mu m \), respectively. It is clear from these images that the field rapidly decreases with height, so keeping a minimum distance between the diamond and the superconducting surface is rather important.

In particular, we would like to simulate the signal obtained with a diamond having a 200 nm NV layer and assuming no gap between the diamond and the superconductor (this is feasible if the superconducting material is deposited directly on the diamond plate). Note that we have assumed a much thicker layer in comparison to the 10 nm layer used in the experiment described in Sec. (4.2). This increases the number of probed NV centers, and is therefore expected to improve the shot-noise limited magnetic sensitivity [see Eq. 2.9].

The enhancement of the signal (namely collecting more fluorescence) is of great importance since the size of the pixel used to resolve a single vortex will have to be much smaller that its size in the former experiment. However, two limiting factors inhibit the NV layer from
being too thick. The first is the magnetic gradient across the layer which introduces inhomogeneous broadening thereby decreasing the sensitivity. The second is the size of the vortex and the separation between vortices, which dictate the minimal required spatial resolution. The thickness of the NV layer may not be larger than the required spatial resolution. Since according to our calculations, a $\sim 1 \mu m$ resolution is required for single vortex imaging, a $\sim 200 \text{ nm}$ NV layer should not limit vortex visibility, while improving our SNR by a factor of 4.5 in comparison to the $\sim 10 \text{ nm}$ NV layer used in the former experiment.

Next, we have simulated the expected vortex magnetic field distribution. We have considered an effective CCD pixel size of 400 nm and assumed that the NV density is $\sim 1 \text{ ppm}$, corresponding to a $\sim 20 \text{ nm}$ separation between every defect and its nearest neighbour. Integrating the vortex field given in Eq. (4.4) experienced by NV centers located between $z = 0 \text{ nm}$ and $z = 200 \text{ nm}$ and separated from each other by $\sim 20 \text{ nm}$, we find the field distribution in Fig. 4.8(c). The corresponding simulated ODMR spectrum is shown in Fig. 4.8(d) where we also show a zero-field ODMR signal for reference. These results indicate the feasibility of single vortex imaging with a diamond sensor under the proposed conditions.

4.3.2 Chip fabrication

In this section we describe the fabrication of a chip for vortex imaging. We have chosen a pattern of four YBCO squares with varying sizes ranging from $5 \mu m$ to $150 \mu m$. This pattern will generate boundary conditions for the magnetic field of the vortices, which we will
Figure 4.8: (a-b) The distribution of the magnetic field above a single vortex. The field is calculated for $z = 0$ (a) and $z = 1 \mu m$ (b). It is clear from the images that the field decays rapidly with height. (c) The integrated magnetic field between $z = 0$ and $z = 200$ nm. We see that, although the field distribution is broadened, the vortex is still detectable. (d) An ODMR signal integrated over a 400 nm pixel. The zero-field signal is exhibited for reference.

map using our magnetometer. The small square may also enable us to capture a single vortex. The fabricated chip is shown in Fig. 4.9.

Square masks were written on the YBCO layer using a mask aligner. A photoresist was then deposited onto the sample [see Fig. 4.9(a)]. This technique is usually referred to as positive mask deposition. Next, we exposed the chip to light and wet-etched it using phosphoric acid at a concentration of 8% for 60 s (etching rate of 5 nm/s). We then deposited a negative mask on the chip by writing the same pattern of squares used previously and subsequently applying the photoresist. At this point, the photoresist is found everywhere except on the squares [see Fig. 4.9(b)]. After exposure of the resist,
we deposited a 100 nm layer of silver on the chip using an electron gun. This layer protects the YBCO layer (e.g. from oxidation) and reflects the green light used for NV sensing (to prevent heating of the superconducting thin film). Lifting off the photoresist, we obtain the desired pattern, as shown in Fig. 4.9(c-d).

**Figure 4.9:** Different stages in the fabrication of the superconductor chip. (a) The smallest square on the chip after the first photoresist deposition. To realize a pattern on the MgO substrate, we used a positive mask and etched the YBCO with phosphoric acid. The cut corners are an artifact of the exposure process. (b) Following the YBCO etching, we covered the chip with a photoresist after writing a negative mask. In this image of one of the squares, the surface is covered with photoresist except for the desired pattern. A minor misalignment of \( \sim 2 \mu m \) can be observed. (c) Image of the final chip, after covering it with silver and lifting off the photoresist. The small square is marked with an arrow since it is hardly visible on this scale. (d) Zoomed image of two of the squares. The actual sizes, measured by microscope, proved to be somewhat smaller than the planned ones (25 \( \mu m \) and 75 \( \mu m \)).
4.4 Conclusions and outlook

We have conducted magnetic field measurements above a thin-layer superconductor using a diamond magnetometer. Using a 10 nm layer of NV centers formed via nitrogen implantation and annealing, we have measured the superconducting phase transition, as well as the local penetration field of vortices. We also determined the surface density of vortices in the layer following a cooling procedure with a field of $B \approx 10$ G.

This work (now submitted for publication in Physical Review B) has opened the road to NV magnetic sensing in integrated devices. In several talks given in 2013 by researchers from the community, this work was heralded as a major achievement. Possible applications are expected to range from high Tc superconductors all the way to the study of neural networks.

For future work, we constructed a superconductor chip which is suitable for vortex mapping. Assuming the density of vortices measured here, a standard optical resolution ($\sim 500$ nm in our case) will be sufficient to map the distribution of vortices in the sample. Compared to our current setup this task will demand a short sample-diamond distance ($< 1 \mu$m) and a detection setup based on a camera or on a high-bandwidth scanning system. These two tasks are the subject of ongoing experimental efforts.

To image the core of a vortex we would require sub-diffraction imaging methods. Such sub-diffraction imaging methods have previously been used with NV centers (see Ref. [130], for example). Imaging of vortex patterns and cores with nanoscale resolution and better
than 1\(\mu\)T sensitivity should therefore be possible with this technology.
Chapter 5

Summary

During my Ph.D research I was walking along two paths. The first path (described in Chapter 3) involved the exploration of several phenomena affecting the performance of magnetic sensors based on NV center ensembles in diamond. Among these phenomena are the sensitivity of the NV magnetic resonance to temperature fluctuations and the effect of exciting light polarization on the emitted fluorescence level. In addition, we present in this chapter how using appropriate experimental techniques such as an efficient red photon collection scheme and look-in based detection may enhance the sensor’s sensitivity. Finally, we have measured our magnetic probe sensitivity. In the process, we have tried to improve the sensor performance utilizing our previous results, and found a sensitivity of $1 \times 10^{-6} \text{T}/\sqrt{\text{Hz}}$. Given that the work was performed in an unshielded environment we believe that random magnetic field fluctuations are the main noise source in the system. The calculated shotnoise limit of the sensor is much better (by $\sim 4$ orders of magnitude) from the measured sensitivity, and we therefore believe that appropriate technical improvements may dramatically enhance our sensor’s performance.
The second research path (described in Chapter 4) was to use NV sensors to image magnetic vortices above superconductors. This task is of high importance for several research efforts going on today such as the search for superconductivity at room temperature. As NV sensors have exhibited a high spatial resolution, we believe they are good candidates to image the hundreds of nm sized vortices. In addition, NV sensors have high sensitivity, and their operation doesn’t damage the superconducting layer as some of the other methods do.

In our work we have developed samples with a thin NV centers layer, and presented first results for magnetic imaging of a superconducting thin layer of the type YBCO. We have monitored the phase transition of the layer, and the penetration field of vortices into the sample. We have also demonstrated flux trapping in the layer, which is due to the existence of vortices, even when the external field is completely shut down. The next step of the research, which is now being worked on, is to improve our imaging system to achieve a resolution of several hundred nm, so as to image individual vortices. At the same time we are developing wide field of view imaging to image the vortex lattice and dynamics.
Bibliography


[37] G. Balasubramanian, I. Y. Chan, R. Kolesov, M. Al-Hmoud, J. Tisler, C. Shin, C. Kim, A. Wojcik, P. R. Hemmer,


[56] P. M. Morse, Phys. Rev. 34, 57 (1929).


[122] E. Hecht, Optics (Addison-Wesley, 2002).


Sensitive Magnetometry Based on NV Centers in Diamonds

Author: Amir Waxman

A thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Physics Department

Submitted to the Senate of Ben-Gurion University of the Negev

Approved by the advisor:

Approved by the Dean of the Kreitman School of Advanced Graduate Studies:

January 15th, 2014

Beer-Sheva
מצהרת תלמיד המחבר עם הגשת עבודת הדוקטור ל審評

אני החתום מטה

מצהיר /

ה בזאת :

אנא סמן :

chiיברתי את חיבורי בעצמי , להוציא עזרת ההדרכה שקיבלתי מאת מנהיגי/ות

החומר המדעי הנכלל בעבודה זו הינו פרי מחקרי/ת מחקרי/ות בשיתוף

בעבודה נכלל חומר מחקרי שהוא פרי שיתוף עם אחרים , למעט עזרה טכנית

ל퍼ח שאושרה על ידם ונמצאת בשדים

תאריך :
15.1.2014

שם התلمיד :
אמיר וקסמן

שנת הלימודים : 2014.15
הע班车 נעשתה בהדרכת
פרופסור רון פולמן
במחלקה לפיסיקה
בפקולטה למדעי הטבע
מגנטומטריה רגישה עם مركز צבע על בסיס חנקן ביהלומים

מחקר לששسيلHoly קריסן שול הרדיום�ולקלה תואר "דוקטור לפילוסופיה"העבש מיקום של כל ארבעת סולות תואר "דוקטור לפילוסופיה"

מאית

אמיר

וקסמן

הוגש לסיןואט אוניברסיטת בן גוריון בנגב

ארוג המנהה

15.1.2014

באד שבע
מגנטומטריה רגישה עם מרכזי צבע על בסיס חנקן ביהלומים

מחקר לשם מילוי חלקי של הדרישות לקבלת תואר "דוקטור לפילוסופיה"

מאט

אmir

ורהש לסיניוטי אתואר פילוסופיה בון גוריון בנגב

15.1.2014

י“ב טבת תשע“ד

באה שבע
Magnetometry with NV Centers: A High-Sensitive Approach Using Color Centers in Ytterbium Barium Copper Oxide

Amir Waksman

In recent years, the NV (NV centers) color centers in Ytterbium Barium Copper Oxide (YBCO) have proven themselves as a versatile and precise system for quantum computing applications, including the study of quantum states and phenomena.

In this thesis, we focus on magnetometry with NV centers characterized by high sensitivity, as well as high spatial resolution.

During my PhD research, I dealt with the topic of building an experimental system that includes an optical microscope, a cryogenic system based on liquid helium, and a control system.

Furthermore, the diamond sample was designed specifically for this work, in particular for studying superconductors. Additionally, we used optical detection magnetic resonance (ODMR) techniques to study the NV centers' magnetic sensitivity.

In conclusion, we studied several factors affecting the ODMR signal, such as the light source power, the optical system efficiency, and the excitation wavelength.

For a superconducting layer of YBCO, we found a critical temperature of 70.0 ± 0.2 Kelvin and initial vortex formation in an external magnetic field of 46.2 ± 3.9 Gauss. Moreover, we showed that optical detection magnetometry can be a feasible method for studying superconductors.