**UNIVERSIDADE DE SÃO PAULO
INSTITUTO DE FÍSICA DE SÃO CARLOS**

Lucas Nunes Sales de Andrade

**Optical measurements of electron spin coherence of
nitrogen-vacancy centers in diamond**

São Carlos

2021

Lucas Nunes Sales de Andrade

**Optical measurements of electron spin coherence of
nitrogen-vacancy centers in diamond**

Dissertation presented to the Graduate Program in Physics at the Instituto de Física de São Carlos da Universidade de São Paulo, to obtain the degree of Master in Science.

Concentration area: Basic Physics

Advisor: Prof. Dr. Sérgio Ricardo Muniz

Corrected version

São Carlos

2021

I AUTHORIZE THE REPRODUCTION AND DISSEMINATION OF TOTAL OR PARTIAL COPIES OF THIS DOCUMENT, BY CONVENTIONAL OR ELECTRONIC MEDIA FOR STUDY OR RESEARCH PURPOSE, SINCE IT IS REFERENCED.

Andrade, Lucas N. S. de
Optical measurements of electron spin coherence of
nitrogen-vacancy centers in diamond / Lucas N. S. de
Andrade; advisor Sérgio Muniz - corrected version -- São
Carlos 2021.
75 p.

Dissertation (Master's degree - Graduate Program in
Basic Physics) -- Instituto de Física de São Carlos,
Universidade de São Paulo - Brasil , 2021.

1. Quantum sensors. 2. Nitrogen-vacancy centers. 3.
Electron spin coherence. I. Muniz, Sérgio, advisor. II.
Title.

To my whole family, in special my parents Francisca and Sales, my brothers Wagner and Vanderlei. To my girlfriend Larissa and my son Gabriel.

ACKNOWLEDGEMENTS

Esse trabalho só foi possível com a ajuda de uma série de pessoas. Queria agradecer, primeiramente, meu orientador Sérgio Ricardo Muniz pelos ensinamentos, pela paciência, pela dedicação e por sempre confiar em mim. Muito obrigado. Queria agradecer também o pessoal do laboratório. São muitas pessoas, mas queria agradecer especialmente ao Dr. Charlie (que, tecnicamente, não faz mais parte do laboratório, mas sempre me ajudou e me apoiou. Sem ele, esse trabalho não teria acontecido), à Thalyta (nossa grande chefe do laboratório) que se tornou uma grande amiga e conselheira, ao Pedro, Mario e todos os outros pelas risadas e momentos bons. Vocês são incríveis.

Queria agradecer também aos meus amigos de graduação: Cris, Lucas, Flávia, Nicolas, Fuu (Nicole) e muitos outros. Aos meus amigos do alojamento que conheci lá em 2015: Letícia, Melise, Andréia, Vitor e Perdi (Jader). Ao Fernando, Felipe e Júnior que moraram comigo. E aos meus amigos de São Paulo: Larissa, Isabelle e Igor. Muito obrigado pelos bons momentos, risadas, pela companhia e por me aturarem.

Não deixaria de agradecer também à minha família, em especial minha mãe Francisca, meu pai Sales e meus irmãos Vanderlei e Wagner. Muito obrigado por me apoiarem, por me motivarem, por estarem sempre junto comigo. Eu amo muito vocês.

Queria agradecer minha namorada Larissa, que nesses últimos meses foi meu porto seguro, me incentivando, me apoiando e me fazendo muito feliz (e que nesse momento está carregando nosso filho Gabriel). Amo vocês.

Por último, queria agradecer as agências de fomento: CAPES, CNPq e FAPESP pela ajuda financeira.

“Life is like riding a bicycle. To keep your balance, you must keep moving.”
Albert Einstein

ABSTRACT

ANDRADE, L. N. S. **Optical measurements of electron spin coherence of nitrogen-vacancy centers in diamond**. 2021. 75p. Dissertation (Master in Science) - Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, 2021.

Among the possible defects that can occur in diamonds, one that draws attention is the nitrogen-vacancy (NV) center. Studied since the early 90s, in recent years, they became one of the most promising platforms for field applications of quantum technology at room temperature, especially for quantum sensing. They are sensitive to electric and magnetic fields, temperature, and strain, making these nanosensors a versatile platform for many applications. The NV center's spin state is easy to read and manipulate by optical means, and, most interestingly, it works well at room temperature, which facilitates its use. The great challenge to implement quantum protocols and quantum algorithms is the coherence time of the quantum states. The NV center stands out for having relatively high coherence times at room temperature. This dissertation presents measurements to characterize the electron spin coherence of NV centers in an ultrapure sample of diamond designed for quantum sensing applications. These measurements combine optical and magnetic resonance techniques. For that, a method was implemented using a conventional CCD camera and a clever imaging protocol, making it possible to perform various pulsed microwave experiments on the electron spin, such as Rabi oscillations and Hahn spin-echo, which were used for determining the characteristic relaxation times (T_1 and T_2). Results show that this system provides at least two readily accessible qubits that can be used in quantum protocols even at room temperature.

Keywords: Quantum sensors. Nitrogen-vacancy centers. Electron spin coherence.

RESUMO

ANDRADE, L. N. S. **Medidas ópticas de coerência de spin eletrônico de centros de nitrogênio-vacância em diamantes**. 2021. 75p. Dissertação (Mestrado em Ciências) - Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, 2021.

Dentre os possíveis defeitos que podem ocorrer nos diamantes, um que chama a atenção é o centro nitrogênio-vacância (NV). Estudados desde o início dos anos 90, nos últimos anos, eles se tornaram uma das plataformas mais promissoras para aplicações de campo da tecnologia quântica em temperatura ambiente, principalmente para sensoriamento quântico. Eles são sensíveis a campos elétricos e magnéticos, temperatura e deformação, tornando esses nanosensores uma plataforma bastante versátil para muitas aplicações. O estado de spin do centro NV é de fácil leitura e manipulação por meios ópticos e, o mais interessante, funciona bem em temperatura ambiente, o que facilita seu uso. O grande desafio para implementar protocolos e algoritmos quânticos é o tempo de coerência dos estados quânticos. O centro NV se destaca por ter tempos de coerência relativamente altos à temperatura ambiente. Esta dissertação apresenta medidas de caracterização da coerência do spin eletrônico de centros NV em uma amostra ultrapura de diamante projetada para aplicações de sensoriamento quântico. Essas medições combinam técnicas ópticas e de ressonância magnética. Para tanto, foi implementado um método utilizando uma câmera CCD convencional e um astuto protocolo de imagem, que possibilita a realização de diversos experimentos pulsados de micro-ondas no spin do elétron, como oscilações de Rabi e spin-eco de Hahn, que foram utilizados para determinação dos tempos característicos de relaxação (T_1 e T_2). Os resultados mostram que esse sistema fornece pelo menos dois qubits prontamente acessíveis que podem ser usados em protocolos quânticos, mesmo em temperatura ambiente.

Palavras-chave: Sensores quânticos. Centro nitrogênio-vacância. Coerência de spin eletrônico.

LIST OF FIGURES

Figure 1 – a) NV center in the diamond lattice. In gray, carbon atoms from the lattice, in blue carbon atoms from NV, in green the nitrogen atom and the blank space represents the vacancy. b) The different possible orientations of the center within the lattice. c) Quantization axis (red vector) of the center defined by the vector which connects the vacancy (white circle) to the nitrogen atom (blue circle). Gray circles represents the carbon atoms.	24
Figure 2 – Electronic structure of the GS.	27
Figure 3 – The radiative paths are denoted by solid arrows. The dashed (- -) arrows represent strong non-radiative decay paths, point-dash (-.-) denotes weak non-radiative paths and dotted (...) is the microwave separation.	29
Figure 4 – A pure state $ 0\rangle$ can be produced after some cycles. Around $180 \mu\text{s}$ (vertical dashed line) of illumination there is a constant photoluminescence (PL) indicating the spin polarization. The green line represents the acousto-optic modulator activation and in red is the fluorescence emitted by the sample.	30
Figure 5 – ODMR spectrum with no external fields. One can notice the degeneracy breaking of $ \pm 1\rangle$ due to presence of strain. $E = 6.7 \pm 0.2 \text{ MHz}$. . .	31
Figure 6 – The external magnetic field $\mathbf{B}$ projection into NV axis defined as z . . .	32
Figure 7 – ODMR spectrum showing the separation between $ \pm 1\rangle$ states due to Zeeman effect. One can notice the presence of 8 peaks due to the four different orientations of the center in the diamond lattice.	33
Figure 8 – ODMR spectrum around 3111 MHz . One can see the separation of around 3 MHz due to Hyperfine interaction.	34
Figure 9 – Energy levels of a nuclear spin $I = 1/2$ coupling with an electronic spin $S = 1/2$. Solid arrows represents allowed transitions and dashed arrows represents forbidden ones.	44

Figure 10 – Micro strip antenna with "omega" shape to increase the MW magnetic field.	46
Figure 11 – Scheme of the microwave system. The microwave produced by the synthesizer goes to IQM that produces orthogonal pulses controlled by the SpinCore digital board, which also controls the microwave pulses. . . .	46
Figure 12 – Schematic view of the circuit to (de)activate the AOM. A home-build circuit controls the amplitude and frequency of the RF signal, the RF signal is conducted to a fast switch that receives a TTL signal from the spincore. The RF signal is amplified and goes to AOM.	47
Figure 13 – Showing the delay of approximately 165 ns between the TTL signal from the digital card SpinCore signal (blue) and AOM activation (green). . . .	48
Figure 14 – The 532 nm beam produced by the laser passes through the AOM, controlled by the SpinCore, which causes a diffraction pattern. The first order diffraction is selected using an iris and a pair of lenses collimates the light beam. A dichroic reflects green light wavelengths and transmits red ones. The photoluminescence emitted by the diamond it's captured by a CCD camera.	49
Figure 15 – Out of scale representation of the optical setup.	50
Figure 16 – Engineered sample of ultrapure diamond with ultrathin NV layer. . . .	50
Figure 17 – ODMR spectra under a field of $ B = 91.69 \pm 0.03$ G (left). The frequency chosen to perform the pulse sequences was 3111.5MHz which is equivalent to a magnetic field $B_z = 85.28 \pm 0.07$ G. The peak can be seen in details on the right side image.	52
Figure 18 – Microwave pulse sequence scheme for all three images.	52
Figure 19 – a) Rabi experiment data with the added MWP (red line) and LAP (green line) images. b) Normalized Rabi experiment data, each point is made of around 30000 MW pulses.	54
Figure 20 – a) Pulse sequence to measure Rabi oscillation. b) Representation on Bloch sphere. c) Experimental (blue) and fitted (black) data. T_2^* for 40 dBm was determined as 190 ns. d) A closer look at the minimum photoluminescence to determine the π -pulse.	55

Figure 21 – Rabi oscillations for different values of power, a) At 40 dBm and b) At 30 dBm. One can notice that the π pulse and T_2^* is dependent on the power applied.	56
Figure 22 – a) Fluorescence intensity (a.u) across the image data, the right figure is a crop of 4x4 pixels of the left one, which has 60x60 pixels. b) Rabi oscillation analysis of the 4x4 pixels image, the coherence time is larger, $T_2^* = 318$ ns, as predicted.	57
Figure 23 – a) <i>Spacial variation of T_2^*</i> . By performing the Rabi analysis for each pixel of the image it was possible to determine how the relaxation time T_2^* varies in the space. One can notice that in the upper right corner the time is 800 ns, which indicates that the magnetic field is more uniform. b) <i>Spacial variation of π-pulse</i> . In the upper right corner the π -pulse is higher, up to 50 ns, which indicates that this is, or it is close to, the center of the antenna where the MW magnetic field is weaker.	58
Figure 24 – a) Scheme of the pulse sequence to measure the longitudinal relaxation time T_1 . b) Representation of the spin (red vector) on Bloch sphere. . .	59
Figure 25 – Longitudinal relaxation time data (red) and the exponential fit (black). The spin-lattice relaxation time was calculated as $T_1 = (0.56 \pm 0.02)$ ms. . .	60
Figure 26 – Plot of relaxation time $1/T_1$ with temperature using Eq. (5.1) with the parameters $A_1 = 0.15$, $A_2 = (2.1 \pm 0.6)10^3 \text{ s}^{-1}$, $A_3 = (2.2 \pm 0.5)10^{-11} \text{ K}^{-5}\text{s}^{-1}$ and $\Gamma = 73 \pm 4 \text{ meV}$. Blue dashed horizontal line represents the relaxation time found in (1) and red dashed horizontal line represents the relaxation time determined in this dissertation. . . .	61
Figure 27 – Longitudinal relaxation time data (green) and the exponential fit (black). This measurements corresponds to a MW power of 30 dBm, with a π -pulse of 88 ns. The fitting provides $T_1 = (0.56 \pm 0.02)$ ms.	62
Figure 28 – Longitudinal relaxation time data (blue) and the exponential fit (black). The MW power here is 26 dBm, resulting in a π -pulse of 120 ns, the same value used in reference (1). The calculated relaxation is $T_1 = (0.57 \pm 0.03)$ ms.	63
Figure 29 – a) Scheme of Hahn Echo pulse sequence to measure the transversal relaxation time T_2 . b) Representation of the spin (red vector) on Bloch sphere. Blue arrows represents dephasing between the spins.	65

Figure 30 – Transversal relaxation time data (red) and the fit (blue). The spin-lattice relaxation time was calculated as $T_2 = (2.38 \pm 0.04) \mu s$ 66

LIST OF ABBREVIATIONS AND ACRONYMS

AOM	Acousto-optic Modulator
APD	Avalanche photodiode
ES	Excited State
ESEEM	Electron Spin Echo Envelope Modulation
FID	Free Induction Decay
GS	Ground State
IQM	IQ Modulator
ISC	Intersystem-Crossing
MW	Microwave
NV	Nitrogen-Vacancy
ODMR	Optically Detected Magnetic Resonance
PL	Photoluminescence
PMT	Photomultiplier
QIP	Quantum Information Processing
QST	Quantum State Tomography
QT	Quantum Thermometer
RF	Radio frequency
SC	Scattering Circuit
TTL	Transistor-Transistor Logic

VCO	Voltage controlled oscillator
VVA	Voltage Variable Attenuators
ZFL	Zero Phonon Lines
ZFS	Zero Field Splitting

CONTENTS

1	INTRODUCTION	21
2	NITROGEN-VACANCY CENTERS	23
2.1	NV center Hamiltonian	24
2.2	Optical pumping and state initialization	28
2.3	Optically Detected Magnetic Resonance	29
3	SPIN DYNAMICS (THEORY)	35
3.1	Microwave Interaction	35
3.2	Rabi Oscillations	38
3.3	Spin-lattice Relaxation	39
3.4	Spin-spin Relaxation	41
4	EXPERIMENTAL SETUP	45
4.1	Microwave generation	45
4.2	Optical System	45
5	MEASUREMENTS OF SPIN COHERENCE	51
5.1	Image Protocol	51
5.2	Rabi Oscillations and T_2^*	53
5.3	T_1 characterization	58
5.4	T_2 characterization	64
6	CONCLUSION	67
	REFERENCES	71

1 INTRODUCTION

Nitrogen-vacancy (NV) centers in diamond have become in recent years a solid state spin qubit for quantum information processing. (1–5) Besides its quantum information processing applications, the NV center is an emerging platform for quantum metrology devices. It has a lot of potential for room temperature nanoscale magnetometry (6–11), bio-magnetometry (12–14), electrometry (15–17), nanoscale thermometer (18–20) and quantum cryptography as a photostable single photon source (21, 22). The center was also a platform to perform experiments for quantum and condensed matter theory as Bell state violation (23) and quantum process tomography (24). These works show how interesting and powerful this system is.

These applications are possible due to some special properties (2):

- A photostable strong optical transitions which allows the detection of individual centers.
- Magnetically resonant and controllable ground state, which can be manipulated using microwaves.
- Long coherence times and coupling between the electronic spin and the nuclear spin from the neighbor nuclei.
- Optical polarization and spin read out at room temperature.

One of the challenges to implement quantum information processing and quantum protocols is that the spin state has to be coherent to allow its manipulation. Usually the system requires ultralow temperatures (25) to achieve long coherence times. The NV center is an alternative to this problem due to an easy spin read out and manipulation by optical means at room temperature.

The main goal of this dissertation is the characterization of the spin-coherence times: *Longitudinal relaxation* T_1 also called spin-lattice relaxation time and the *Transversal relaxation* T_2 also called spin-spin relaxation time, of an engineered sample of ultrapure diamond.

More precisely, the dissertation follows:

Chapter 2 provides a brief introduction about the nitrogen-vacancy center, its electronic structure and the dynamic spin process involved. It is explained how one can use microwaves and optical pulses to prepare and read out spin states. This chapter presents a description of the main technique implemented in this work: Optically Detected Magnetic Resonance as well.

Chapter 3 presents a description of how the microwave interacts with the NV center ground-state. There is an introduction about the spin-coherence times and their main mechanisms. It also describes how the experiments are performed using a special microwave pulse sequence.

Chapter 4 describes the experimental setup used in our studies. A complete description of the optical setup is given in addition with the sample preparation. The microwave generation is also covered.

Chapter 5 contains the main results and discussions for the spin coherence times, the longitudinal relaxation $T_1 = 0.56 \pm 0.03$ ms, the transversal relaxations $T_2 = 2.38 \pm 0.04$ μ s and $T_2^* = 350$ ns, $T_2^* = 190$ ns at 30 dBm and 40 dBm respectively.

2 NITROGEN-VACANCY CENTERS

A pure diamond is composed only by carbon atoms that are arranged in a repeating pattern called face-centered cubic (fcc) lattice structure. Being a semi-conductor, the diamond contains a large energy gap of 5.47 eV (at 300 K) between the conduction and the valence bands which makes it transparent in the visible part of the spectrum. However, with the presence of defects, such as nitrogen (Type Ia and Ib diamond type classification) and boron (Type IIb diamond), it may become colorful, giving rise to the so-called color centers. (13,26)

The most common defect is the nitrogen one. It can be embedded in the diamond lattice by replacing one carbon atom, this defect is called P1 center and is not optically active, acting as an electron donor in the crystal. (1) If the N impurity is associated to a vacancy it becomes optically active and is called nitrogen-vacancy color center.

The Nitrogen-Vacancy (NV) center is a point defect in the diamond lattice characterized by a nitrogen-vacancy pair along $[111]$ (crystal coordinate) direction (27) with C_{3v} symmetry, which implies 120° symmetrical rotation along the quantization axis, that is defined by the vector which connects the nitrogen to the vacancy, see Fig. (1.c). As written before, the diamond has a fcc lattice structure, this allows four different NV orientations, which in crystal coordinates are given by $[111]$, $[\bar{1}\bar{1}1]$, $[\bar{1}1\bar{1}]$ and $[1\bar{1}\bar{1}]$ as shown in Fig. (1.b).

The center can be found in two different charge states: NV_0 and NV_- , distinguished by their Zero Phonon Lines (ZFL): 2.156 eV (575 nm) for NV_0 and 1.945 eV (637 nm) to NV_- (28,29). The neutral NV_0 center contains five electrons which occupy the dangling bonds of the nitrogen and carbon atoms neighboring the vacancy (2,30), this results in an electronic spin $S = 1/2$. The negatively charge NV_- contains six electrons, where this last electron is from the surrounding lattice (probably other nitrogen). (30) This results in an electronic spin $S = 1$. In this dissertation we will work with the negatively charge one, referring to it just as NV.

Figure 1 – a) NV center in the diamond lattice. In gray, carbon atoms from the lattice, in blue carbon atoms from NV, in green the nitrogen atom and the blank space represents the vacancy. b) The different possible orientations of the center within the lattice. c) Quantization axis (red vector) of the center defined by the vector which connects the vacancy (white circle) to the nitrogen atom (blue circle). Gray circles represents the carbon atoms.

Source: By the author.

2.1 NV center Hamiltonian

To understand the spin properties of the center, semi-empirical molecular model of deep level defects in semiconductors (30–34) and *ab initio* (35–38) calculations were done. In this dissertation, there will be only a qualitative description of the ground state Hamiltonian with its main terms.

The electron spin is mostly influenced by spin-spin and Zeeman interaction. The effective NV center Ground State (GS) Hamiltonian, in the presence of a static magnetic field, in a coordinate system with the z axis along the quantization axis, can be written as follows (39):

$$H = H_{ZF} + H_{Ze} + H_{HF} + H_{Zn} + H_{QP}. \quad (2.1)$$

The first term on the right side of the equation is due to dipole interaction by the unpaired electrons. This interaction lifts the degenerescence of GS. It is called Zero Field

Splitting (ZFS) and it can be written as:

$$H_{ZF} = \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}, \quad (2.2)$$

where $\mathbf{S}$ is the total spin and $\mathbf{D}$ is a diagonal and traceless matrix that represents the dipolar interaction which is written as

$$D = \begin{pmatrix} D_{xx} & 0 & 0 \\ 0 & D_{yy} & 0 \\ 0 & 0 & D_{zz} \end{pmatrix}, \quad (2.3)$$

one can define D_j as D_{jj} for simplicity. Thus, H_{ZF} is given by

$$H_{ZF} = D_x S_x^2 + D_y S_y^2 + D_z S_z^2, \quad (2.4)$$

that can be rewritten as

$$H_{ZF} = \frac{(D_x + D_y)}{2} (S_x^2 + S_y^2 + S_z^2 - S_z^2) + \frac{(D_x - D_y)}{2} (S_x^2 - S_y^2) + D_z S_z^2. \quad (2.5)$$

Once D is traceless, then one can write $(D_x + D_y)/2 = -D_z/2$. Leading to

$$H_{ZF} = D \left(S_z^2 - \frac{S(S+1)}{3} \right) + E (S_x^2 - S_y^2), \quad (2.6)$$

where $D = 3D_z/2$ and $E = D_x - D_y$.

The second term of Eq. (2.1) is the electron Zeeman interaction, where the electronic spin couples with the magnetic field $\mathbf{B}$, one can write it as

$$H_{Ze} = \gamma_e \mathbf{B} \cdot \mathbf{S}, \quad (2.7)$$

where $\gamma_e = 28 \text{ GHz/T}$ is the gyromagnetic ratio of NV electron spin.

The third term of Eq. (2.1) describes the hyperfine interaction, where the electron spin $\mathbf{S}$ interacts with the nuclear spin $\mathbf{I}$ of the nitrogen atom. It is write as

$$H_{HF} = \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} = A^{\parallel} S_z I_z + A^{\perp} [S_x I_x + S_y I_y], \quad (2.8)$$

where $A^{\parallel}$ and $A^{\perp}$ are the axial and non-axial hyperfine parameters. The nuclear spin is different for each isotope, ^{14}N has $I = 1$ and ^{15}N has $I = 1/2$. The result is a splitting of $m_s = 1$ into $\pm 1/2$ and $m_s = -1$ into $\mp 1/2$ for ^{15}N , as shows Fig. (2).

The fourth term of Eq. (2.1) is the nuclear Zeeman coupling, which is similar to the usual Zeeman interaction, but instead of electronic spin it is the nuclear spin $\mathbf{I}$ that couples with $\mathbf{B}$. It is given by

$$H_{Zn} = -\gamma_I \mathbf{B} \cdot \mathbf{I}. \quad (2.9)$$

Here γ_I denotes the nuclear gyromagnetic ratio of nitrogen.

The last term of Eq. (2.1) denotes the Quadrupolar Nuclear Interaction. For nuclear spins $I > 1/2$ there is a coupling between the electric quadrupole of the nucleus and the electric field gradient produced by charges distributions in the vicinity of the center. It can be written as

$$H_{QP} = \mathbf{I} \cdot \mathbf{P} \cdot \mathbf{I}, \quad (2.10)$$

where $\mathbf{P}$ denotes the quadrupole tensor, one can rewrite as

$$H_{QP} = P \left(I_z^2 - \frac{I(I+1)}{3} \right). \quad (2.11)$$

$P \approx -4.96$ MHz is the quadrupole nuclear splitting (40).

There are two different isotopes of nitrogen: ^{14}N , (99.6% abundance) and ^{15}N (0.4%) (1, 41). The effective Hamiltonian will be different for each of isotope, for ^{14}N , it is given by:

$$\begin{aligned} H = & D \left(S_z^2 - \frac{S^2}{3} \right) + E(S_x^2 - S_y^2) + \gamma_e \mathbf{B} \cdot \mathbf{S} + A^{\parallel} S_z I_z + \\ & A^{\perp} [S_x I_x + S_y I_y] - \gamma_I \mathbf{B} \cdot \mathbf{I} + P \left(I_z^2 - \frac{I^2}{3} \right). \end{aligned} \quad (2.12)$$

The hyperfine parameters are $A^{\parallel} = -2.14 \pm 0.07$ MHz and $A^{\perp} = -2.70 \pm 0.07$ MHz (40, 42). The nuclear gyromagnetic ratio is $\gamma_I \approx 3.1$ MHz/T. (43)

For the ^{15}N there is no quadrupole interaction, since $I = 1/2$, thus

$$H = D \left(S_z^2 - \frac{S^2}{3} \right) + E(S_x^2 - S_y^2) + \gamma_e \mathbf{B} \cdot \mathbf{S} + A^{\parallel} S_z I_z + A^{\perp} [S_x I_x + S_y I_y] - \gamma_I \mathbf{B} \cdot \mathbf{I}. \quad (2.13)$$

The hyperfine parameters are given by $A^{\parallel} = 3.03 \pm 0.03$ MHz and $A^{\perp} = 3.65 \pm 0.03$ MHz. The nuclear gyromagnetic ratio in this case is $\gamma_I \approx -4.3$ MHz/T. (42–44) The ZFS constant is the same for both isotopes and is given by $D = 2.87$ GHz at room temperature and for low temperatures regimes (<10 K) $D = 2.88$ GHz (43).

The electronic structure of the GS can be seen in Fig. (2). It shows the splittings caused by ZFS, Zeeman and hyperfine couplings.

Figure 2 – Electronic structure of the GS.

Source: By the author.

2.2 Optical pumping and state initialization

When a defect is stable within the diamond, new energy levels arise inside the diamond bandgap. The defect can be excited using an appropriate light source and the excited electron can result in an emission of a zero phonon line (ZPL), thus, qualitatively, the NV center can be imagined as a isolated "atom" within the diamond lattice containing its own energy levels.

As said before, the negatively charge NV center has electronic spin $S = 1$, the main models describe the electronic structure of the NV center containing four energy levels (2): a triplet ground state 3A_2 , a triplet excited state 3E and two intermediate metastable states 1A_1 and 1E , see Fig. (3).

Before the optical pumping, the GS triplet is approximately equally populated following the Maxwell-Boltzmann distribution. Under optical illumination by off resonance, i.e photon with energy greater than 1.945 eV, usually 532 nm green light. There is an excitation from the ground state 3A_2 to the excited state (ES) 3E ($^3A_2 \rightarrow ^3E$). The excitation is spin conservative, following the dipolar selection rules, but the decay is strongly spin dependent.

When the ES spin state is $|0\rangle$ the decay is mostly via a radiative 637 nm band emission, with life time of 12.9 ± 0.1 ns (45) and low probability of intersystem-crossing (ISC) with the intermediate state 1A_1 . When the ES spin state is $|\pm 1\rangle$, there is a greater than 50% probability for ISC to the intermediate state via a non-radiative path ($^3E \rightarrow ^1A_1$). The decay from 1A_1 state to 1E is approximately instantaneous 0.9 ± 0.5 ns (46) with two possible paths of approximately equal probabilities: one radiative infrared band emission 1.190 eV, that is only visible under optical illumination (47), and one non-radiative. The second metastable state 1E has a life time that is temperature dependent, ranging from 462 to 142 ns (46, 48) and there is a new ISC to GS ($^1E \rightarrow ^3A_2$) that will populated preferably the $|0\rangle$ state. The whole spin dynamics can be seen in Fig. (3). Because of the greater life time of the intermediate states (≈ 300 ns), when the ES state is $|\pm 1\rangle$, the decay rate will be slower when compared to $|0\rangle$. Thus, $|\pm 1\rangle$ will give less fluorescence in the beginning of an optical excitation which allows the ability for optical readout of the spin state.

One interesting property of the NV center is the ability to, after just a few cycles

Figure 3 – The radiative paths are denoted by solid arrows. The dashed (- -) arrows represent strong non-radiative decay paths, point-dash (-.-) denotes weak non-radiative paths and dotted (...) is the microwave separation.

Source: By the author.

under optical illumination, create a pure $|0\rangle$ state, since the spin dynamics preferably populates $|0\rangle$. The creation of the pure state is indicated by a constant fluorescence rate as shows Fig. (4).

The spin dynamics described above enables the ability for optical readout of the spin and the optical initialization of the spin state which are features of interest to quantum information processing.

2.3 Optically Detected Magnetic Resonance

To drive the spin states $|0\rangle \rightarrow |\pm 1\rangle$, in the absence of external fields, one can use microwave (MW) with frequency of $D = 2.87 \text{ GHz}$ that resonates with the states. This electron-magnetic resonance will be perceive as a downcrease in the photoluminescence, thus, there is an Optically Detected Magnetic Resonance (ODMR) and varying the MW frequency one can identify the resonances corresponding to those states. The PL dependence with MW frequency is called ODMR spectrum.

Because of the presence of strain, the degenerescence of the $|\pm 1\rangle$ states of GS is

Figure 4 – A pure state $|0\rangle$ can be produced after some cycles. Around $180 \mu\text{s}$ (vertical dashed line) of illumination there is a constant photoluminescence (PL) indicating the spin polarization. The green line represents the acousto-optic modulator activation and in red is the fluorescence emitted by the sample.

Source: By the author.

lifted. In this case the ODMR spectrum will have two peaks, see Fig. (5) and the resonance frequency in this case is given by Eq. (2.14).

$$\nu_{\pm} = D \pm E, \quad (2.14)$$

with E given in MHz.

When an external magnetic field $\mathbf{B}$ is applied, the Zeeman shifts leads to a further separation between the $|\pm 1\rangle$ states. In this case, the new resonance frequency is

$$\nu_{\pm} = D \pm \sqrt{E^2 + \gamma_e^2 B_z^2}, \quad (2.15)$$

where B_z is the field projection on the NV axis, see Fig. (6). If the projection of the magnetic field $\mathbf{B}$ in NV axis is much larger than E , i.e, $\gamma_e B_z \gg E$, one can neglected

Figure 5 – ODMR spectrum with no external fields. One can notice the degenerescence breaking of $|\pm 1\rangle$ due to presence of strain. $E = 6.7 \pm 0.2$ MHz.

Source: By the author.

the strain term, thus, the new resonance frequency will be

$$\nu_{\pm} = D \pm \gamma_e B_z, \quad (2.16)$$

where the frequency difference between $|\pm 1\rangle$ states is given by

$$\Delta\nu = 2\gamma_e B_z. \quad (2.17)$$

As mentioned earlier, due to C_{3v} symmetry and the lattice structure of the diamond, four different possible orientations of NV center are possible. Therefore, there will be four different $\mathbf{B}$ projections, leading up to eight resonance frequencies, depending on the orientation. An example of ODMR spectrum with an applied external magnetic field can be seen in Fig. (7).

The NV center is sensitive to electric and magnetic fields, temperature and strain. The analysis of the ODMR spectrum can, in principle, determine these physical quantities,. For example, the measurement of the splittings between the peaks can be used to determine the magnetic field vector $\mathbf{B}$ which produced these separations.

Figure 6 – The external magnetic field $\mathbf{B}$ projection into NV axis defined as z .

Source: By the author.

To calculate the magnetic field vector is necessary to write the four crystal orientations of the diamond, which are given by (1)

$$\hat{u}_1 = \frac{\hat{i} + \hat{j} + \hat{k}}{\sqrt{3}}, \hat{u}_2 = \frac{-\hat{i} - \hat{j} + \hat{k}}{\sqrt{3}}, \hat{u}_3 = \frac{\hat{i} - \hat{j} - \hat{k}}{\sqrt{3}} \text{ and } \hat{u}_4 = \frac{-\hat{i} + \hat{j} - \hat{k}}{\sqrt{3}}, \quad (2.18)$$

and corresponds to $[111]$, $[\bar{1}\bar{1}1]$, $[1\bar{1}\bar{1}]$ and $[\bar{1}1\bar{1}]$, respectively.

Due to the symmetry of the crystal

$$\hat{u}_1 + \hat{u}_2 + \hat{u}_3 + \hat{u}_4 = 0. \quad (2.19)$$

The applied magnetic field interaction can be described mathematically by projecting the $\mathbf{B}$ vector on the equation above which leads to

$$\mathbf{B} \cdot \hat{u}_1 + \mathbf{B} \cdot \hat{u}_2 + \mathbf{B} \cdot \hat{u}_3 + \mathbf{B} \cdot \hat{u}_4 = 0, \quad (2.20)$$

where $\mathbf{B} = B_x \hat{i} + B_y \hat{j} + B_z \hat{k}$.

The magnetic field vector than can be determined by using the Eqs. (2.17) and (2.20), associating each separation with one different projection of the magnetic field on the NV axis. This will lead to a system of four different equations which can be used to

Figure 7 – ODMR spectrum showing the separation between $|\pm 1\rangle$ states due to Zeeman effect. One can notice the presence of 8 peaks due to the four different orientations of the center in the diamond lattice.

Source: By the author.

determine $\mathbf{B}$ in the laboratory frame. In our case, using the data from the Fig. (7), the magnetic field is

$$\mathbf{B} = [44.32 \pm 0.02, 27.98 \pm 0.02, 75.23 \pm 0.02] \text{ G}, \quad (2.21)$$

which give us a magnetic field $|B| = 91.69 \pm 0.03 \text{ G}$.

Taking a closer look on the ODMR spectrum, around 3111 MHz that corresponds to the frequency to drive $|0\rangle \rightarrow |1\rangle$, one can observe the lifting due to hyperfine coupling of $3.24 \pm 0.09 \text{ MHz}$. The hyperfine interaction breaks the $|1\rangle$ into $|\pm 1/2\rangle$, see Fig. (8)

Since the center is sensitive to magnetic fields, electric fields and temperature, the analysis of the ODMR spectra allows one, in principle, to determine these values. Thereby, one of the main applications of this platform is as a magnetic sensor. It was proposed for nanoscale sensor to DC, AC and fluctuating magnetic fields. These applications can use one or more of the three possibles architectures: single NV centers in nanodiamonds, an array of individual NV centers in a bulk crystal and an ensemble of NV in a bulk crystal substrate (2). The spatial resolution and sensitivity are ruled by: the proximity of the

Figure 8 – ODMR spectrum around 3111 MHz. One can see the separation of around 3 MHz due to Hyperfine interaction.

Source: By the author.

center with the sample, the ground state coherence time and the number of centers in the sensing volume (7,8). Isotopically pure diamond and dynamic decoupling techniques yield magnetic field sensitivities of single centers as high as $4 \text{ nT}/\sqrt{\text{Hz}}$. (2,6)

3 SPIN DYNAMICS (THEORY)

To perform quantum protocols and quantum information processing (QIP) it is important to know the characteristic relaxation times of the spin states since these protocols must be done while the spins are coherent. These times can be summarized in:

- T_1 : Longitudinal Relaxation Time or spin-Lattice relaxation time. T_1 is the characteristic time for the system to reach thermal equilibrium. In solids, it is the result of Raman interaction with lattice phonons at room temperature. In NV ensembles the T_1 typical order is around 1 – 10 ms. (1)
- T_2 : Transversal Relaxation Time or spin-spin relaxation time. T_2 is the characteristic time for homogeneous spin dephasing. It is dependent on NV location and its environment.
- T_2^* : It is similar to T_2 but for magnetic field inhomogeneities. When the electronic spin interacts with the nuclear spin-bath of carbon atoms (^{13}C), a fluctuating non-zero magnetic field interacts with the electron spin, leading to decoherence. Other mechanisms may also be a source of decoherence, e.g strain, temperature and fluctuations on the external magnetic field. The details will be discussed later on this chapter.

The general time scale is given by

$$T_1 \geq T_2 > T_2^*, \quad (3.1)$$

where T_2^* is always shorter than T_2 and T_2 can be less or equal to T_1 .

3.1 Microwave Interaction

To characterize the times T_1 , T_2 and T_2^* , it is important to see how the microwave interacts with the electronic spin of the NV center. Assuming a rotating wave in xy plane which corresponds to the microwave and a static magnetic field in z-direction that

corresponds to the external magnetic field, the resulting magnetic field vector can be written as

$$\mathbf{B} = [B_{mw} \cos(\omega_{mw}t + \phi), B_{mw} \sin(\omega_{mw}t + \phi), B_z], \quad (3.2)$$

where B_z is the external static field, B_{mw} is the magnetic field of the microwave with angular frequency ω_{mw} and ϕ is a arbitrary phase.

To simplify the analysis of MW interaction, one can neglect the hyperfine (≈ 3 MHz) and the nuclear Zeeman (≈ 50 kHz) terms, since their energies are small compared to the large axial $D = 2.87$ GHz. Thus, the simplified Hamiltonian^{*}, in the S_z basis, can be written as

$$H = DS_z^2 + \gamma_e B_z S_z + \gamma_e B_{mw} [S_x \cos(\omega_{mw}t + \phi) + S_y \sin(\omega_{mw}t + \phi)]. \quad (3.3)$$

The Hamiltonian above is written in the laboratory frame of reference and in this frame, the electronic spin does a precession around B_z which is parallel to the NV axis. To simplify the calculus, the Hamiltonian given in (3.3) can be rewritten in the microwave frame of reference. In this new frame, the observer rotates with frequency ω_{mw} around the z axis and the spin seems to be static. If $|\psi\rangle$ is the state at the laboratory frame, in the rotating frame the new state is given by $|\sigma\rangle = R|\psi\rangle$, where $R = e^{-i\omega_{mw}S_z t}$ is an unitary transformation i.e $RR^\dagger = 1$.

In the rotating frame, the new Hamiltonian can be determined using the following equation:

$$\hat{H} = RHR^\dagger + i\dot{R}R^\dagger, \quad (3.4)$$

which leads to

$$\begin{aligned} \hat{H} = & R[DS_z^2 + \gamma_e B_z S_z + \gamma_e B_{mw} (S_x \cos(\omega_{mw}t + \phi) + S_y \sin(\omega_{mw}t + \phi))]R^\dagger \\ & + i(i\omega_{mw}S_z)RR^\dagger, \end{aligned} \quad (3.5)$$

^{*} Because of the sample used in the experiments, throughout this section it is used only the Hamiltonian given by Eq. (2.13) which is related to the ^{15}N isotope. More details in Chapter 4.

once R commutes with S_z and R is unitary transformation, then

$$\begin{aligned}\hat{H} = & DS_z^2 + \gamma_e B_z S_z + \omega_{mw} S_z + \gamma_e B_{mw} [\cos(\omega_{mw}t + \phi) R S_x R^\dagger] \\ & + \gamma_e B_{mw} [\sin(\omega_{mw}t + \phi) R S_y R^\dagger],\end{aligned}\quad (3.6)$$

which can be rewritten as

$$\hat{H} = DS_z^2 + \gamma_e B_z S_z + \omega_{mw} S_z + \gamma_e B_{mw} [S_x \cos(\phi) + S_y \sin(\phi)], \quad (3.7)$$

where it was used the rotating wave approximation and the following formula

$$R S_x R^\dagger = S_x \cos(-\omega_{mw}t) + S_y \sin(-\omega_{mw}t), \quad (3.8)$$

$$R S_y R^\dagger = S_y \cos(-\omega_{mw}t) - S_x \sin(-\omega_{mw}t). \quad (3.9)$$

The microwave phase is arbitrary, then, one can consider that $\phi = 0$. Thereby, in matrix format, the Hamiltonian is given by

$$\hat{H} = \begin{pmatrix} D + \gamma_e B_z + \omega_{mw} & \frac{\gamma_e B_{mw}}{\sqrt{2}} & 0 \\ \frac{\gamma_e B_{mw}}{\sqrt{2}} & 0 & \frac{\gamma_e B_{mw}}{\sqrt{2}} \\ 0 & \frac{\gamma_e B_{mw}}{\sqrt{2}} & D - \gamma_e B_z - \omega_{mw} \end{pmatrix}. \quad (3.10)$$

To make transitions $|0\rangle \leftrightarrow |\pm 1\rangle$, the diagonal entries have to be null. Therefore, the resonance frequency is given when $\omega_0 \pm \omega_{mw} = 0$, that is, when the microwave frequency matches the angular frequency ω_0 given by Eq. (2.16).

Since $\hat{H}$ is time independent, the time evolution operator will be given by

$$U(t) = e^{-i\hat{H}t} = e^{-i\vec{n}\cdot\vec{S}}. \quad (3.11)$$

At resonance, $\vec{n}$ is given by $\vec{n} = (\omega_1 t, 0, 0)$, where $\omega_1 = \gamma_e B_{mw}$ is called nutation frequency and $\vec{S} = (S_x, 0, 0)$. Thus, Eq. (3.11), can be written as

$$U(t) = \exp[-i\omega_1 S_x t], \quad (3.12)$$

which corresponds to a rotation around the x-axis by an angle $\theta = \sqrt{\omega_1 t}$. Thus, the interaction with MW can be seen as a rotation of the spin vector around some axis, which in this case is the x-axis.

In the case of $\phi \neq 0$, the spin will rotate around the axis defined by

$$\hat{n} = \cos(\phi)\hat{x} + \sin(\phi)\hat{y}. \quad (3.13)$$

The equation above shows that changing the MW phase ϕ , one can rotate the spin in any direction, for example, setting $\phi = \pi/2$, leads to $\vec{n} = \hat{y}$, which is orthogonal to x-axis, thus, controlling the phase of the pulse, one can create MW pulses that are orthogonal to each other. This is very useful for some protocols of quantum information processing where it is necessary to perform different logic gates which are composed of rotations along different axes.

3.2 Rabi Oscillations

As seen in the previously section, the interaction with MW causes a rotation of the spin vector around a defined axis given by Eq. (3.13). In the case where $\omega_{mw} = \omega_0$ and $\phi = 0$, the spin rotates around x-axis with frequency $\Omega_R = \omega_1$ which is called Rabi frequency. If the system is out of resonance ($\omega_{mw} \neq \omega_0$), the frequency of oscillation will be given by the generalized Rabi frequency $\Omega'_R = \sqrt{\omega_1^2 + \Delta^2}$, where $\Delta = \omega_0 - \omega_{mw}$ is called detuning.

In Chapter 2, it was seen that the PL signal $\mathcal{S}$ is proportional to spin state, being greater when the state is $|0\rangle$ and lower when $|\pm 1\rangle$. When MW is applied at resonance, i.e. $\omega_{mw} = \omega_0$, it drives transitions $|0\rangle \leftrightarrow |\pm 1\rangle$ with the frequency $\Omega_R = \omega_1$. Applying MW for different times τ drives the system to a state $|\psi\rangle$ which signal $\mathcal{S}$ is proportional to the population difference between the states $|0\rangle$ and $|\pm 1\rangle$ and given by the projection of $|\psi\rangle$ into the eigenstate $|0\rangle$. Thus, the probability of finding the system in this specific state is

$$\mathcal{S} \propto \sin^2\left(\frac{\Omega_R t}{2}\right), \quad (3.14)$$

where it was considered that the detuning is null, $\Omega'_R = \Omega_R$.

The oscillations do not go on indefinitely. The presence of magnetic field inhomogeneities causes a dephasing of the spins within the sample which results in a decay of the PL signal characterized by the coherence time T_2^* , so, the PL signal will be given by

$$\mathcal{S} \propto (e^{-t/T_2^*}) \sin^2 \left(\frac{\Omega_R t}{2} \right). \quad (3.15)$$

It is important to perform Rabi oscillations measurements because it gives information about the system's coherence time (T_2^*) and characterizes the π -pulse which is defined as the time interval of MW interaction to invert the population $|0\rangle \rightarrow |1\rangle$ or $|0\rangle \rightarrow |-1\rangle$ depending on the MW frequency applied, indicated by the minimum PL signal.

Once the π -pulse is characterized, one can also apply MW for a shorter time interval, thus obtaining the so-called $\pi/2$ -pulse, defined as the half of the π -pulse time. This pulse generates the coherence state between $|0\rangle$ and $|1\rangle$, being widely used in several quantum protocols.

Both pulses, π and $\pi/2$ pulses, will be used to measure the coherence times T_1 and T_2 , the details will be discussed in the next sections.

3.3 Spin-lattice Relaxation

As seen before, the MW application produces transitions between the states $|0\rangle \leftrightarrow |\pm 1\rangle$. Considering that the MW frequency is such that one makes the transition $|0\rangle \leftrightarrow |1\rangle$, the NV center can be considered as a two level system. Defining n_0 as the spin population of $|0\rangle$ at any moment and n_1 as the spin population of $|1\rangle$, the difference between $|0\rangle$ and $|1\rangle$ populations defines the spin temperature T_s (49)

$$\frac{n_1}{n_0} = \exp \left[\frac{-h\nu_1}{kT_s} \right], \quad (3.16)$$

where $\nu_1 = D + \gamma_e B_z$ and k is the Boltzmann constant.

In thermal equilibrium, the population of the states will be given by

$$\frac{N_1}{N_0} = \exp \left[\frac{-h\nu_1}{kT_0} \right], \quad (3.17)$$

where T_0 is the ambient temperature.

At equilibrium, the spin temperature will be equal to the ambient temperature, i.e, $n_0 = N_0$ and $n_1 = N_1$. In order to reach this equilibrium, the system must interact with its surroundings. The transitions will be induced by thermal fluctuations that causes molecular motion. In solids this process happens through lattice vibrations (phonon interaction) that leads to relaxation. This relaxation can happen in different ways

- Direct process: A phonon the from lattice with energy $h\nu_1$ can be absorbed ($|0\rangle \rightarrow |1\rangle$) or emitted ($|1\rangle \rightarrow |0\rangle$) by the NV center ground state which leads to a transfer of populations. This is called first order process, because it involves just one phonon.
- Raman process: A phonon of any frequency ν_p interacts with the NV center causing an up $|0\rangle \rightarrow |1\rangle$ or down $|1\rangle \rightarrow |0\rangle$ transition and is scattered with a different frequency $\nu_p \mp \nu_1$. This is called a second order process because it involves two phonons.
- Orbach process: This process involves the absorption of a phonon by a direct process to excite the system to a higher level, at an energy Γ which is related to the energy of local vibrations modes of the NV center within the diamond lattice. Phonons at frequencies $\Gamma, \Gamma - h\nu_1$ causes up and down transitions by two phonon process. This process is strongly temperature dependent, being determined by the number of phonons of energy Γ .

Because it involves two phonons, the Raman and Orbach process have a smaller coupling compared with direct process, but they may play the major role in the relaxation. This happens because at ambient temperature $h\nu_1 \ll kT_0$, i.e the thermal energy is much larger than the gap between the states, the number of phonons at $h\nu_1$ is low. The Raman process can involve any phonon of any energy not being limited by phonons of energy $h\nu_1$ and Orbach process depends on the number of phonons with energy Γ , that for the NV center can be as high as 74 meV.

The process of relaxation is not instantaneous, considering that $\Delta n = n_0 - n_1$ is the population difference at a given time t and $\Delta N = N_0 - N_1$ is population difference in

thermal equilibrium, the rate equation for the relaxation process can be written as (49)

$$\frac{d(\Delta n)}{dt} = \frac{1}{T_1}[\Delta N - \Delta n], \quad (3.18)$$

where T_1 is the spin-lattice relaxation time. The solution of the equation above is

$$\Delta n(t) = \Delta N + C_1 e^{-t/T_1}, \quad (3.19)$$

where C_1 is a constant related to the population difference at $t = 0$.

Before the optical spin polarization into $|0\rangle$, the system is in thermal equilibrium with the populations following Eq. (3.17). The optical pumping produces the pure state $|0\rangle$ and, once pumping is stopped, that is, the laser is off, the system reaches thermal equilibrium after a time T_1 following Eq. (3.19).

To measure T_1 , it is necessary to, after the optical spin polarization, apply a π -pulse to invert the populations ($|0\rangle \rightarrow |1\rangle$). The PL signal, which measures the projection of the spin in z-direction and is proportional to the population difference between the states, will follow an exponential decay, according to

$$\mathcal{S} \propto e^{-t/T_1}. \quad (3.20)$$

Therefore, to measure T_1 , after the initialization, one simply apply a π -pulse, and measure the PL signal for different times τ to obtain the behavior shown in Eq. (3.20).

3.4 Spin-spin Relaxation

As discussed before, after the optical polarization the spin is on $|0\rangle$ state. In the rotating frame this is represented by a spin vector static and along z-direction. When one applies a $\pi/2$ -pulse along the x-axis, the spin vector will rotate to xy plane, whose final result is a spin vector in the negative direction of y-axis. If the microwave frequency is different from the resonance frequency, i.e, $\omega_{mw} \neq \omega_0$, the spin vector will do a precession about z-axis with frequency $\Delta = \omega_0 - \omega_{mw}$.

In a NV sample, each center is under different conditions due to local fluctuations of the magnetic field. The main cause of these fluctuations are: spin-spin interactions between

the electronic and the nitrogen's nuclear spin; inhomogeneities of the external magnetic field; interaction of the electronic spin with the nuclear spin-bath of carbon atoms (^{13}C); temperature fluctuations; strain gradient and other spins (50). So, each electronic spin will have a slightly different resonance frequency, thus a different precession frequency. This leads to a loss of coherence between the spins that are in xy plane, which attenuates monotonically the transversal component that results in an exponential decay of the PL signal. In addition to these factors, when a measurement is performed, the final result is actually an average about all centers in the sample which further decreases the coherence time.

To compensate the dephasing caused by these fluctuations, one can use a special dynamical decoupling technique called spin echo, first implemented by Hahn (51). The principle of dynamical decoupling is to make a sequence of MW pulses that refocus any accumulated phase.

To simplify the study of the Hahn echo sequence, one can consider that, in first order, the interaction with the magnetic field fluctuations can be described by an effective magnetic field $B_{eff}(t)$. (41) The NV center Hamiltonian, neglecting hyperfine interaction, can be written as

$$H = DS_z^2 + \gamma_e(\mathbf{B}_{static} + \mathbf{B}_{eff}(t)) \cdot \mathbf{S}, \quad (3.21)$$

where B_{static} is the static magnetic field and $\mathbf{S}$ is the spin operator. Since $D = 2.87 \text{ GHz}$, in first order, the non-axial interactions can be neglected, then

$$H = DS_z^2 + \gamma_e(B_{z \text{ static}} + B_{z \text{ eff}}(t))S_z. \quad (3.22)$$

When the spins that are in a superposition state $\psi = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle)$ freely evolve for a time interval τ , assuming a resonant MW excitation, each of them will have acquired an accumulated phase given by

$$\phi = \int_0^\tau 2\pi\gamma_e B_{z \text{ eff}}(t) dt. \quad (3.23)$$

In the Hahn Echo sequence, a π -pulse is applied after a time interval τ which gives an echo of the spin at 2τ . This π -pulse inverts the sign of the acquired phase leading to

(41)

$$\phi = \int_0^\tau 2\pi\gamma_e B_{z_eff}(t)dt + \int_\tau^{2\tau} -2\pi\gamma_e B_{z_eff}(t)dt. \quad (3.24)$$

If the magnetic field varies slowly it can be considered a constant, leading to

$$\phi = 2\pi\gamma_e B_{z_eff}\tau - 2\pi\gamma_e B_{z_eff}\tau = 0. \quad (3.25)$$

The efficacy of the refocusing depends on how slow the magnetic field fluctuations are compared to the free precession interval.

Varying the free precession time τ one can observe a decay of the echo amplitude that is characterized by the time constant T_2 . One interesting fact is that often the decay is accompanied by periodic falls and rises. This have been termed Electron Spin Echo modulation (ESEEM) which the most common reason for appearance is the electron-nuclear interactions in the spin system. (52)

Qualitatively, the ESEEM may be explained by considering the electron-nuclear transitions in the system consisting of a nuclear spin $I = 1/2$ which interacts with an electron spin $S = 1/2$, both at a constant magnetic field. This system has four energy levels and, in general the splitting of two levels with $m_s = +1/2$ ($h\nu_a$) differs from the splitting of the level with $m_s = -1/2$ ($h\nu_b$). Four Electron Spin Resonances (ESR) transitions are possible, see Fig. (9). Two of them, occur without any change in the value of the projection of the nuclear spin which are called allowed transitions (represented as solid arrows), and the other two, represented as dashed arrows, are accompanied by a simultaneous change in the projection of the nuclear spin and are called forbidden. (52)

Taking into account all the transitions between the levels, the interference between the various basis states makes the amplitude of the echo signal to be dependent on the phase factors $\exp[\pm i(E_1 - E_2)\tau/\hbar]$, $\exp[\pm i(E_3 - E_4)\tau/\hbar]$ and $\exp\{\pm i[(E_1 - E_2) \pm (E_3 - E_4)]\tau/\hbar\}$, where E_1, E_2, E_3 and E_4 are the energies of each state. This leads to a variation of the echo amplitude as a function of the time τ , which is the free precession time, and the frequencies $\nu_{a,b}$ and $\nu_a \pm \nu_b$.

The theoretical treatment of the nuclear modulation effect is based on the spin density operator formalism. More detail can be found in (1). The modulation and the

Figure 9 – Energy levels of a nuclear spin $I = 1/2$ coupling with an electronic spin $S = 1/2$. Solid arrows represents allowed transitions and dashed arrows represents forbidden ones.

Source: By the author.

relaxation time constant can be determined fitting the data with the following equation

$$\mathcal{S}(\tau) = e^{(-2\tau/T_2)^n} \left\{ 1 - \frac{k}{4} [2(\cos(\omega_a\tau) - 1)(\cos(\omega_b\tau) - 1)] \right\}, \quad (3.26)$$

where ω_a, ω_b are the angular frequencies of the nuclear transitions, k depends on the external magnetic field $\mathbf{B}$, T_2 is the coherence time and n is a power index which varies depending on the decoherence mechanism.

Thus, the measurement of T_2 is done performing the Hahn echo sequence which can be summarized in $(\pi/2 - \tau - \pi - \tau - \pi/2)$, where the last $\pi/2$ -pulse is necessary to project the NV spin into z-axis to do the measurement.

4 EXPERIMENTAL SETUP

4.1 Microwave generation

To make transitions between the states $|0\rangle \rightarrow |\pm 1\rangle$ and to perform ODMR experiments it is necessary to use microwaves. To do so, a frequency synthesizer SIGNAL GENERATOR SG384 was used. This equipment produces a sinusoidal signal from DC up to 4 GHz and maximum power of 16.5 dBm. The signal is sent to an IQ modulator (IMOH-01-458 1542) (IQM). The IQM consists of three digital IN-ports: LOAD, I and Q, and an OUT-port. The MW signal is conducted to the LOAD port, the OUT signal can be In-phase (with I port activated) or in Quadrature (90° phase shift) (Q port activated) relative to the initial one. A TTL (Transistor-Transistor Logic) signal from a fast digital board (SpinCore Pulso Blaster, PBESR-PRO-300), which has a time resolution of 3.3 ns, controls the I and Q ports, thus controlling the phase of the OUT signal. In this way, one can produce MW pulses that are orthogonal to each other.

After the IQM there is a fast switch (CMCCS0947A-C2), which also receives a TTL signal, this switch controls the MW on and off. After the switch, the MW signal is conducted to a preamplifier (Mini Circuits ZX60-8008E-S+), which increases the power in approximately 10 dB, and finally to an amplifier (Mini Circuits ZHL-16W-43-S+) that increases it 45 dB. To increase the Rabi frequency, an antenna with an "omega" shape was built, as shown in Fig. (10). The smaller radius intensifies the MW magnetic field B_{mw} in that region which increases the Rabi frequency.

To avoid any damage to the equipment, specially with the amplifier, it was used a circulator (Circulator CS 3000) with a $50\ \Omega$ heavy-duty load. A scheme of the system can be seen in Fig. (11).

4.2 Optical System

The optical pumping and state reading is provided by a green 532 nm laser (Thorlabs, DJ532-40) and depending on the purposes of the experiment, it is necessary to have a pulsed laser beam, e.g. to perform MW pulse sequence like Hahn echo, Rabi, etc. or have the laser continuously to make the ODMR spectrum. In order to control the on

Figure 10 – Micro strip antenna with "omega" shape to increase the MW magnetic field.

Source: By the author.

Figure 11 – Scheme of the microwave system. The microwave produced by the synthesizer goes to IQM that produces orthogonal pulses controlled by the SpinCore digital board, which also controls the microwave pulses.

Source: By the author.

and off of the laser, it was used an Acousto-optic Modulator (AOM) (AOMO 3110-320). The AOM consists of a crystal and a piezoelectric transducer, that is activated with a radio frequency (RF) signal. The RF causes a vibration in the transducer which produces an acoustic wave in the crystal, causing a diffraction pattern on the laser beam. A dedicated electronic circuit controls the frequency (Voltage controlled oscillator (VCO), Mini-circuits, ZX95-200-S+) and amplitude (Voltage Variable Attenuators (VVA), Mini-circuits, ZX73-2500-S+) of the RF. The RF signal is sent to a switch (Mini-circuits, ZASWA-2-50DR+) which is also controlled by the digital board (PBESR-PRO-300). The RF signal is amplified (Mini-circuits, ZHL-03-5WF) and finally goes to the AOM. See Fig. (12). Choosing the correct frequency and power, one can make the first order diffraction to be maximized, and, using an iris, select it. Thus, the AOM(de)activation provides the control of laser on and off. More details in (1).

Figure 12 – Schematic view of the circuit to (de)activate the AOM. A home-build circuit controls the amplitude and frequency of the RF signal, the RF signal is conducted to a fast switch that receives a TTL signal from the spincore. The RF signal is amplified and goes to AOM.

Source: By the author.

The delay and response time of the AOM is related with its position in relation to the laser beam. To perform the microwave pulse sequences is important to determine its value for the pulse sequence be performed correctly. The device was positioned in such a way that the delay and response time, i.e, the instant between the TTL signal from the digital card and the activation of AOM, which turn the laser on, was around 165 ns as shown in Fig. (13).

The AOM causes the diffraction pattern, as described previously, and an iris selects first order diffraction. A pair of lenses with 25 mm and 5 mm focal length respectively, were used to expand and collimate the beam to around 10 mm of diameter. The beam is reflected by a mirror and separated by a dichroic (SemRock, Di02-R561-25x36), which reflects light with wavelength shorter than 561 nm. The reflected laser beam goes to an objective lens (Apochromat 50x-0,95 NA) and to the diamond. The fluorescence emitted by the diamond is collected by the same objective and passes right through the dichroic. Another lens was positioned to form an image on the camera. A filter (FELH0550) was used to block any green light that may pass through the dichroic, allowing only the fluorescence to reach the camera.

At the end there is a CCD camera (POINT GREY FL3-FW-0S1M-C) to capture the fluorescence. Fig. (14) shows a scheme of the setup. One could use a spectrometer or a photomultiplier (PMT), depending on the objective, as well. There are some advantages to use a camera instead of a PMT. In magnetometry for example, it is possible to do a pixel-

Figure 13 – Showing the delay of approximately 165 ns between the TTL signal from the digital card SpinCore signal (blue) and AOM activation (green).

Source: By the author.

pixel ODMR spectra, and then calculate the magnetic field in each pixel. In the other hand, for experiments using nanodiamonds with single NV centers, a photo-multiplier may be a better choice because of the low PL intensity.

To produce the Zeeman effect, a strong neodymium magnet was positioned next to the sample. A schematic view can be seen in Fig. (15).

The NV defect can occur naturally (Type Ib diamond) or can be artificially produced. In this work it was used an engineered sample of ultrapure (type IIa) diamond made by chemical vapor deposition (CVD). The surface was irradiated with $^{15}\text{N}^+$ ions at 5 keV and density of $10^{13} \text{ }^{15}\text{N}^+/\text{cm}^2$. This process produced a thin layer of NV centers around 8 to 16 nm below the top surface. After the implantation, the sample was annealed at 800 °C in vacuum to allow the migration and trapping of the vacancies next to the implanted nitrogen. This process converts 0.8% of the implanted nitrogen into NV-, which results in an estimated density around $10^3 \text{ NV}/\mu\text{m}^2$. More details in (1). The crystal is a (100) oriented plate whose edges coincide with axes $[1, 0, 0]$, $[0, 1, 0]$ and $[0, 0, 1]$ which are the lab reference frame. The electronic grade single crystal was thinned and polished to a $2 \times 2 \times 0.1 \text{ mm}^3$ size. See Fig. (16).

The microwave antenna was prepared in-house. A copper film of 100 nm thickness

Figure 14 – The 532 nm beam produced by the laser passes through the AOM, controlled by the SpinCore, which causes a diffraction pattern. The first order diffraction is selected using an iris and a pair of lenses collimates the light beam. A dichroic reflects green light wavelengths and transmits red ones. The photoluminescence emitted by the diamond is captured by a CCD camera.

Source: By the author.

was deposited on one surface of a thin glass plate by sputtering. A printed paper with the circuit was applied on the copper surface using hot iron transfer. To remove the unwanted copper, the plate was put into a chemical etching solution (ferric chloride) for 30 seconds. To remove the ink of the plate it was used a few drops of thinner and water. More details in reference (1).

Figure 15 – Out of scale representation of the optical setup.

Source: By the author.

Figure 16 – Engineered sample of ultrapure diamond with ultrathin NV layer.

Source: SEGURA, C. (1)

5 MEASUREMENTS OF SPIN COHERENCE

This chapter contains the main results for the sequences described in chapter 3. The first step was to determine the resonances frequencies with an ODMR spectrum, since the peak was chosen the pulse sequences were performed and the PL signal was measured using a CCD camera. The imaging protocol devised to achieve this will be described in this chapter as well.

To build the ODMR spectrum the the MW frequency was varied from 2600 to 3140MHz, each data of the ODMR spectrum contains 64 images for each frequency, scanned using steps of 1.0 MHz. In chapter 2 this same spectrum was analyzed using Eqs. (2.18) and (2.20). The magnetic field was determined as $\mathbf{B} = [44.32 \pm 0.02, 27.98 \pm 0.02, 75.23 \pm 0.02]$ G with $|B| = 91.69 \pm 0.03$ G. This magnetic field interacts with the NV center electronic spin yielding to 8 resonances frequencies as shows Fig. (17). One can notice that the PL signal contrast is less than 0.3%.

To perform the pulse sequences, it was chosen the 3111.5 MHz resonance frequency due its higher contrast among the others peaks in the spectrum. This peak can be seen with details in Fig. (17). According to Eq. (2.16) this resonance frequency is equivalent to an effective magnetic field $B_z = 85.28 \pm 0.07$ G along its quantization axis and drives transitions $|0\rangle \rightarrow |1\rangle$ of Zeeman states.

5.1 Image Protocol

It is worth mentioning that the measurements were performed with a CCD camera instead of PMT or avalanche photodiode (APD) as usually found in the literature because of the higher quantum efficiency of the sensor. To perform the measurements a special image protocol was devised in order to optimize the sample illumination and the acquisition rate. Fig. (18) summarizes this protocol. More details in (1).

Once the resonant frequency is fixed, the pulse sequences discussed in chapter 3 followed the same protocol. First it is applied an optical pumping of 300 μ s to produce the pure $|0\rangle$ state and initialize the system. After that, the laser is turned off and the state is manipulated with the MW pulses. Then the PL signal is measured by turning the

Figure 17 – ODMR spectra under a field of $|B| = 91.69 \pm 0.03$ G (left). The frequency chosen to perform the pulse sequences was 3111.5MHz which is equivalent to a magnetic field $B_z = 85.28 \pm 0.07$ G. The peak can be seen in details on the right side image.

Source: By the author.

Figure 18 – Microwave pulse sequence scheme for all three images.

Source: By the author.

laser on, which also does the optical pumping that restarts the system to another MW pulse sequence. The delay and response time of the AOM have to be considered to allow the correct measurement, since the laser needs to be turned on and off at the right time.

The data consists of three different images. The first image contains the microwave pulse sequence (MWP - Microwave photo), e.g. Rabi, Hahn echo etc. In this photo, a laser

pulse of 300 μs is applied and ,after the MW sequence, it is turned on again to restart the process. The second laser pulse is necessary for the diamond to emit fluorescence, which, as described in chapter 2, will be proportional to the population difference between the states $|0\rangle$ and $|1\rangle$. In this single image, the entire protocol described above is done 150 times. The second image is from the background (BGP - Background photo), in which the whole system is turned off. This image is subtracted from the first one. The third image (LAP - Laser photo) contains the same number of sequences as the first one, around 150, but it does not contain the microwave pulses, only the laser ones, it is used for normalization.

For all three images, the camera is maintained open for about 30 to 40 ms to allow the acquisition of sufficient fluorescence light. To plot the data experiment, these three pictures are taken for each time interval τ , for example, in Rabi's experiment the microwave must be applied for different time intervals. So, for each time τ of interaction with MW, the three photos are taken: MWP, BGP and LAP. To reduce noise, this are done from 150 to 200 times.

Finally, for each value of τ , all MWP, BGP and LAP images are added, a example can be seen in Fig. (19.a)) where the red line represents the sum of the MWP images and the green line represents the sum of LAP images. Once added, the normalized data is given by (WMP-BGP)/LAP whose result is shown in Fig. (19.b))

The protocol described above allowed the implementation of the Rabi, Hahn echo and the sequence to measure T_1 , and consolidates a solid basis that will allow the implementation of other several sequences in the future.

5.2 Rabi Oscillations and T_2^*

As described in chapter (3) the MW application can be seem as a rotation of the spin vector around x-axis where the frequency of the rotation is given by the Rabi frequency: $\Omega_R = \gamma_e B_{mw}$. A scheme of the pulse sequence and the representation of the spin vector on Bloch sphere can be seen in Fig. (20).

The first Rabi oscillation experiment was performed with a MW power of 40 dBm, at 3111.5 MHz, which drives the transition $|0\rangle \rightarrow |1\rangle$. Each point in Fig. (20.c) are composed by approximately 30000 MW pulses, which leads to a total of 3 million pulses

Figure 19 – a) Rabi experiment data with the added MWP (red line) and LAP (green line) images. b) Normalized Rabi experiment data, each point is made of around 30000 MW pulses.

Source: By the author.

for one single analysis. The PL signal was measured for MW pulses varying from 0 to 930 ns using the image protocol discussed in the previously section. The data can be seen in Fig. (20.c)). Using Eq. (3.15) the π -pulse was determined as $\tau_\pi = 44$ ns, that can be also determined by the first minimal fluorescence. It is interesting to notice that, performing an intermediate pulse time, e.g, $\tau_{\pi/2} = 22$ ns, which is equivalent to a $\pi/2$ -pulse, one can produce a superposition state $\psi = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle)$ that is crucial for quantum information protocols.

One can notice that the oscillations do not continue indefinitely, see Fig. (20. c)), due to the magnetic field fluctuations discussed in chapter (3) that leads to decoherence. The relaxation constant T_2^* was calculated fitting the data with the Eq. (3.15) as $T_2^* = 190$ ns. It is important to emphasize that this coherence time is given to the whole imaging

Figure 20 – a) Pulse sequence to measure Rabi oscillation. b) Representation on Bloch sphere. c) Experimental (blue) and fitted (black) data. T_2^* for 40 dBm was determined as 190 ns. d) A closer look at the minimum photoluminescence to determine the π -pulse.

Source: By the author.

area which is proportional to the laser beam's size.

A second Rabi oscillation experiment was performed with a different MW power of 30 dBm for comparison. The signals for 40 dBm and 30 dBm in Fig. (21) shows that both π -pulse and T_2^* are power dependent. At 30 dBm the π -pulse was determined as $\tau_\pi = 90$ ns, and $T_2^* = 350$ ns. The π -pulse dependence was already expected, assuming a resonant excitation, the Rabi frequency is given by $\omega_1 = \gamma_e B_{mw}$, a lower MW power implies in a lower MW magnetic field, which decreases the Rabi frequency and leads to a longer time to invert the populations.

The direct dependence of T_2^* with the MW power was not expected. As discussed earlier, the transversal relaxation time is dependent on several mechanisms, and four factors may, together, explain this dependence: the size of the region illuminated by the laser, the shape of the MW antenna, the pulse duration and the fact that the measured

Figure 21 – Rabi oscillations for different values of power, a) At 40 dBm and b) At 30 dBm. One can notice that the π pulse and T_2^* is dependent on the power applied.

Source: By the author.

time is an average of the coherence times across the image.

When a measurement is performed, the result is actually an average of all the centers that were excited by the MW and the laser. When the MW power increases, the duration of the MW pulse becomes shorter, since the Rabi frequency is related to the MW magnetic field. This increases the number of centers excited by the MW due to the broadening of frequency spectrum. Because of the large area being illuminated by the laser, around $180 \mu\text{m}$ of diameter, and, under a large gradient of intensity and direction of magnetic field due to the antenna special shape, when a short MW pulse is applied, more centers with different precession frequencies will be affected compared to a longer one, this implies in more centers dephasing which leads to a shorter coherence time.

To test this hypothesis we can benefit from the fact that we are using a CCD camera, it allows a Rabi analysis to be done in a smaller region, for example, taking a

crop in the fluorescence image as shows Fig. (22.b)). A smaller region contains fewer NV centers, and the MW magnetic field is more uniform, which in theory would increase the coherence time in that region. For a 4x4 pixels cropped image of the original one (which has 60x60 pixels), the Rabi oscillations analysis, see in Fig. (22.b)), resulted in a greater coherence time, as expected, being equal to $T_2^* = 318$ ns.

Figure 22 – a) Fluorescence intensity (a.u) across the image data, the right figure is a crop of 4x4 pixels of the left one, which has 60x60 pixels. b) Rabi oscillation analysis of the 4x4 pixels image, the coherence time is larger, $T_2^* = 318$ ns, as predicted.

Source: By the author.

The CCD camera gives another advantage, that is the analysis pixel by pixel, thus, one can build a coherence map, in which the variation of T_2^* in space is plotted, as shown in Fig. (23.a)). In this figure, the image protocol discussed in section (5.1) was done for each pixel of the original image. One can notice that in the upper right corner the coherence times are longer, reaching up to 800 ns, which indicates that it is the center

of the antenna's "omega", where the MW magnetic field is smaller and more uniform, thus increasing the coherence value. Performing the same pixel by pixel analysis it is also possible to determine how the time to perform the π -pulse varies spatially, the result can be seen in Fig. (23.b)). The result agrees with Fig. (23.a)) as in the upper right corner the pulse time is longer, reaching 50 ns, indicating a less intense MW field.

Figure 23 – a) *Spacial variation of T_2^** . By performing the Rabi analysis for each pixel of the image it was possible to determine how the relaxation time T_2^* varies in the space. One can notice that in the upper right corner the time is 800 ns, which indicates that the magnetic field is more uniform. b) *Spacial variation of π -pulse*. In the upper right corner the π -pulse is higher, up to 50 ns, which indicates that this is, or it is close to, the center of the antenna where the MW magnetic field is weaker.

Source: By the author.

5.3 T_1 characterization

Since the π -pulse was determined, the sequence to characterize T_1 was performed. The representation of the spin vector on Bloch sphere with the pulse sequence scheme can be seen in Fig. (24). After the initialization with a green laser pulse of 300 μ s, a π -pulse was applied to invert the populations and, after a free evolution time τ , the PL signal was measured. The free evolution time was varied from 0 to 5.5 ms and the data can be seen in Fig. (25).

Figure 24 – a) Scheme of the pulse sequence to measure the longitudinal relaxation time T_1 . b) Representation of the spin (red vector) on Bloch sphere.

Source: By the author.

The data was fitted using $\mathcal{S}(t) = A + Be^{-t/T_1}$ and the spin-lattice relaxation time calculated was $T_1 = (0.56 \pm 0.02)$ ms. This result is more than 1 ms below the value determined in (1) (1.78 ± 0.05 ms) where the same sample was used. To study this difference is necessary to analyze the mechanisms that can affect the spin-lattice time

Based on the work (53), where the dependence of T_1 with temperature and magnetic field was studied for three different samples with three different NV center concentrations. One can analyze how the spin-lattice time of the sample utilized in this dissertation varies with temperature. The referenced work considered that, due to ZFS of $D = 2.87$ GHz, the occupation of phonon modes at this frequency is low, therefore, the single-phonon process can be neglected. Thus, the relaxation must be via two-phonon Raman process, with $(1/T_1)_{\text{Raman}} \propto T^5$ (54) and by Orbach process (55), with $(1/T_1)_{\text{Orbach}} \propto (e^{\Gamma/kT} - 1)^{-1}$, where Γ is the local vibrational energy. The authors in (53) show that the data for a wide range of samples was fitted well by the expression

$$\frac{1}{T_1} = A_1 + \frac{A_2}{e^{\Gamma/kT} - 1} + A_3 T^5, \quad (5.1)$$

Figure 25 – Longitudinal relaxation time data (red) and the exponential fit (black). The spin-lattice relaxation time was calculated as $T_1 = (0.56 \pm 0.02) \text{ ms}$.

Source: By the author.

where A_1 is dependent on the sample and proportional to the NV concentration, A_2, A_3 and Γ are parameters common to all samples, and T is the temperature. The equation above shows that for extremely low temperatures the relaxation becomes temperature independent, being ruled only by the NV concentration that is related to A_1 .

The common parameters found were $A_2 = (2.1 \pm 0.6)10^3 \text{ s}^{-1}$, $A_3 = (2.2 \pm 0.5)10^{-11} \text{ K}^{-5}\text{s}^{-1}$ and $\Gamma = 73 \pm 4 \text{ meV}$, that closely matches the energy of the local vibration modes of the NV center. Since the parameters are common for the three samples, it is reasonable that they will be the same for the sample used in this dissertation.

As mentioned before, A_1 is dependent on the sample characteristics, using the values determined in (53) one can write the following relation: $A_1 = 0.354 n^{1.473}$, where n is the concentration of NV centers in the sample, given in ppm (parts per million). To estimate the concentration in ppm of our sample, it was consider that, in the volume corresponding to a layer of NV center of 10 nm high and $1 \mu\text{m}^2$ in area, there are around $1.8 \cdot 10^9$ atoms. (56) For a NV concentration of $10^3 \text{ NV}/\mu\text{m}^2$ this is equivalent to 0.56 ppm which leads to $A_1 = 0.15$. Since A_1 is small, probably the concentration of NV centers makes no difference in the times observed both in this dissertation and in (1).

Using the parameters, A_1, A_2, A_3 and Γ , it was possible to plot the curve of $1/T_1$

corresponding to our sample as shows Fig. (26). The values of T_1 determined in this dissertation and in (1) are represented by horizontal dashed lines, red and blue, respectively. One can notice that even for the relaxation time of 1.78 ms it would be necessary a temperature around 410 K, that is high if compared with room temperature.

Figure 26 – Plot of relaxation time $1/T_1$ with temperature using Eq. (5.1) with the parameters $A_1 = 0.15$, $A_2 = (2.1 \pm 0.6)10^3 \text{ s}^{-1}$, $A_3 = (2.2 \pm 0.5)10^{-11} \text{ K}^{-5}\text{s}^{-1}$ and $\Gamma = 73 \pm 4 \text{ meV}$. Blue dashed horizontal line represents the relaxation time found in (1) and red dashed horizontal line represents the relaxation time determined in this dissertation.

Source: By the author.

Since the laser power and the spot size here and in (1) are comparable, the intensity at the focal plane can be considered equal and it does not explain the result of 0.56 ms. The main difference in the experimental setup between the one used in this dissertation and one used in (1) is the special shape of the antenna. As discussed before, it was built to increase Rabi frequency by increasing the magnetic field in that region. The higher MW power could make the sample hotter in that region, thus decreasing T_1 value.

To analyze this hypothesis, two more measurements of T_1 were performed for lower MW powers of 30 and 26 dBm, the results are shown in Fig. (27) and Fig (28). According to the previous discussion, the time necessary to invert the populations is dependent on the MW power and for 30 dBm the π -pulse was characterized as 90 ns, and for 26 dBm

Figure 27 – Longitudinal relaxation time data (green) and the exponential fit (black). This measurements corresponds to a MW power of 30 dBm, with a π -pulse of 88 ns. The fitting provides $T_1 = (0.56 \pm 0.02)$ ms.

Source: By the author.

the π -pulse was 120 ns. One can notice that the spin-lattice relaxation time did not change for different MW power values: $T_1 = (0.56 \pm 0.02)$ for 30 dBm and $T_1 = (0.56 \pm 0.02)$ for 40 dBm. Only for 26 dBm the result changed: $T_1 = (0.57 \pm 0.03)$, however it is still equivalent to the other two values. This indicates that the MW power does not interfere in the final result.

A factor that could explain the difference between the relaxation times found in this dissertation and in (1), and also the reason both times are shorter than predicted for the sample, of approximately 5 ms, is the laser that is not being fully blocked by the iris when the AOM is deactivated. During the MW sequences described in chapter (3), the laser needs to be turned on and off at the right time for the measurements to be taken correctly. For example, if the laser is turned on earlier than expected in the sequence to determine T_1 , or if it remains on during the measurement, the effective relaxation time will be shorter, since the optical pumping will transfer the population to the state $|0\rangle$. As explained in chapter (4), the laser control is done using the AOM and an iris. When AOM is off the light is not diffracted and is blocked by the iris, so ideally the NV center is not excited. When AOM is activated, the light from the laser is diffracted and the first order of diffraction passes through the iris and goes to the diamond, where the spin dynamics

Figure 28 – Longitudinal relaxation time data (blue) and the exponential fit (black). The MW power here is 26 dBm, resulting in a π -pulse of 120 ns, the same value used in reference (1). The calculated relaxation is $T_1 = (0.57 \pm 0.03)$ ms.

Source: By the author.

process described in chapter (2) takes place.

As stated above, when AOM is turned off, ideally there should be no green light reaching the diamond, since this "escaping" light can excite it and consequently affect the results. The optimal suppression rate, i.e. the difference in the light power between the laser on and off, is 60 dB or more. Using a Scanning-Slit Optical Beam Profiler (BP209-VIS), it was possible to calculate the suppression rate for the current experimental setup, the result was only 22.76 dB, which is approximately 5000 times less than ideal. This unblocked laser is probably exciting the diamond's NV centers and decreasing the value of T_1 . Probably, the suppression rate of the system used in (1) was higher, but not large enough to obtain the predicted value of 5 ms, according to (53), at 300 K.

So far, it is not clear why the relaxation times is shorter than measured in (1), where the same sample was used. This continues to be investigated in our laboratory, to understand what is affecting the system. It is important to emphasize that, although the relaxation is shorter than the predicted, it is large enough to perform several quantum information processing protocols. These protocols are composed by quantum gates, which are essentially rotations of the spin vector around some defined axis, e.g. the Hadamard

gate which creates the superposition state $(|0\rangle + |1\rangle)/\sqrt{2}$ can be done by rotating the spin vector, that was originally at $|0\rangle$, around the y-axis by $\pi/2$ angle. In our system, gates like these, take tens of nanoseconds to be performed, therefore, during $560 \mu\text{s}$, which is the relaxation time of the current system, there could be performed around 11000 gates, which is an expressive number.

5.4 T_2 characterization

The sequence performed to determine T_2 was the Hahn Echo $(\pi/2 - \tau - \pi - \tau - \pi/2)$, see Fig. (29) to visualize the representation of the spin vector on Bloch sphere during this sequence and the MW pulse sequence as well. To determine the relaxation time, the free evolution time τ was varied from 0 to 11000 ns in steps of 50 ns. The data, obtained using the image protocol described in section (5.1), was fitted with Eq. (3.26) and can be seen in Fig. (30)

One can observe a oscillatory modulation signal on top of the expected exponential decay. This modulation oscillation corresponds to the ^{15}N nuclear Larmor precession frequencies: f_a that corresponds to the hyperfine parameter and f_b which corresponds to the Larmor frequency of the nucleus and is dependent on the magnetic field B_z .

Using Eq. (3.26), it was possible to determine $T_2 = (2.38 \pm 0.04) \mu\text{s}$ and the hyperfine parameters due to the modulation on top of the exponential decay. The frequency $f_a = \omega_a/2\pi = (3.04 \pm 0.01) \text{ MHz}$ is equivalent to $A^{\parallel} = 3.0 \text{ MHz}$ and $f_b = \omega_b/2\pi = (70 \pm 30) \text{ kHz}$ corresponds to the Larmor frequency of the nucleus at $B_z = 85.28 \pm 0.07 \text{ G}$. Compared with the literature (2), for samples at room temperature, the T_2 determined is a reasonable value.

The transversal coherence time obtained is large enough to allow different algorithms of quantum information processing at room temperature. The hyperfine coupling in the NV centers also shows that are two different spins (electron and nuclear) that can be manipulated and implemented as qubits in future quantum protocols.

Figure 29 – a) Scheme of Hahn Echo pulse sequence to measure the transversal relaxation time T_2 . b) Representation of the spin (red vector) on Bloch sphere. Blue arrows represents dephasing between the spins.

Source: By the author.

Figure 30 – Transversal relaxation time data (red) and the fit (blue). The spin-lattice relaxation time was calculated as $T_2 = (2.38 \pm 0.04) \mu s$.

Source: By the author.

6 CONCLUSION

In this work, we presented a basic description of the nitrogen-vacancy (NV) center in diamonds, explaining how to manipulate it using microwaves and how to optically read its electronic spin-state using the ODMR technique. It was also shown that the analysis of the obtained ODMR spectrum can be used to make measurements of magnetic fields (magnetometry), and to determine the spin properties of the sample.

The main goal of this dissertation was the measurement of the spin coherence times of an engineered NV sample. To achieve this, a special imaging protocol with a conventional CCD camera was used, instead of APDs or PMTs. Using this protocol, it was possible to perform Rabi oscillations measurements and the MW pulse sequences to determine T_1 and T_2 .

The first step was to determine the resonance frequencies with a ODMR spectrum, among the different transitions it was chosen the peak at 3111.5 MHz due to its higher contrast. Once the frequency was defined the image protocol described in 5 was implemented, it consist on images of the fluorescence in three cases, with the MW pulse sequence applied, with only the lasers pulses and a image of the background, with everything turned off.

The first pulsed experiment was a Rabi sequence. The experiments were performed at different microwave powers: 30 and 40 dBm. According to the data, it was found a relationship between the values of the inhomogeneous dephasing and the power: 190 ns for 40 dBm and 350 ns for 30 dBm. As discussed in chapter (5), a higher MW power implies a smaller microwave pulse, a smaller pulse is wider in the frequency spectrum and excites more centers. Due to the size of the illuminated region which is relatively large, several NV centers under a large magnetic field gradient, both in intensity and direction due to the shape of the "omega" antenna, are being excited. Since the measure is actually an average of all excited centers, more centers implies in a decrease of the overall relaxation time. To test this hypothesis a crop of 4x4 of the original image was done, doing that the effective area would be smaller e consequently the time would increase, and this was exactly what happened, the time increased to 318 ns. We could benefit that we were using

a CCD camera to do a pixel by pixel analysis and thus, construct a coherence map of T_2^* , where were observed coherence times high as 800 ns.

For the longitudinal relaxation, the main sequence can be summarized as $(\pi - \tau)$, where a π -pulse inverts the population $|0\rangle \rightarrow |1\rangle$, and after a time τ the PL signal is measured. From the data the value found was $T_1 = 0.56 \pm 0.02$ ms for a microwave power of 40 dBm. This value is approximately 1.2 ms below the values found in reference (1) where the same sample was use. To investigate the effect of heating caused by the new antenna design, other measurements were performed for different microwave powers at 30 and 26 dBm. The relaxation times determined did not changed significantly, indicating that the MW power does not seem to affect these results. The deviation from the expected behavior is probably related to green light that is not being fully blocked by the iris when the AOM is deactivated, the excitation transfers the population to $|0\rangle$, thus, decreasing the coherence value. Despite that, the observed coherence times are already large enough to implement useful quantum protocols using this device.

The other pulse sequence used was the Hahn echo which can be summarized as $(\pi/2 - \tau - \pi - \tau - \pi/2)$. This pulse sequence compensates the inhomogeneous dephasing with the application of a π -pulse, this pulse inverts the sign of the acquired phase which leads to a refocusing of the spin coherence. Varying the value of the free evolution time τ , it was expected a simple exponential decay of the echo amplitude, but the signal showed a modulation on top of it. This modulation is due to the hyperfine coupling between the electronic spin and the nuclear spin of ^{15}N .

Using analysis provide in (1) it was possible to determine the frequencies of modulation f_a and f_b using Eq. (3.26). The results were $f_a = (3.04 \pm 0.01)$ MHz (corresponding to the hyperfine parameter $A^{\parallel} = 3.0$ MHz) and $f_b = (70 \pm 30)$ kHz which corresponds to the Larmor frequency of the nucleus at $B_z = 85.28 \pm 0.07$ G. Using the same equation it was possible to determine the spin-spin relaxation time as $T_2 = 2.38 \pm 0.04$ μs . This value is consistent with the ones found in the literature for room temperature measurements, and given the observed Rabi frequencies in our system (with gate times on the order of tens of nanoseconds), it shows that even without further dynamical decoupling the room temperature spin coherence is sufficiently long to implement relevant quantum protocols in this sample.

The characterization of these relaxation times is an important step for future experiments related to quantum information processing and for quantum sensing in our laboratory. The fact that the system also has two different spins (nuclear and electronic) that can be manipulated makes it possible to implement more complex and interesting protocols using two qubits.

REFERENCES

- 1 SEGURA, C. O. **Diamond studies for applications in quantum technologies**. 2019. 115 p. Tese (Doutorado em Ciências) — Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, 2019.
- 2 DOHERTY, M. W. *et al.* The nitrogen-vacancy colour centre in diamond. **Physics Reports**, Elsevier, v. 528, n. 1, p. 1–45, 2013.
- 3 WRACHTRUP, J.; JELEZKO, F. Processing quantum information in diamond. **Journal of Physics**, IOP Publishing, v. 18, n. 21, p. S807, 2006.
- 4 NEMOTO, K. *et al.* Photonic architecture for scalable quantum information processing in diamond. **Physical Review X**, APS, v. 4, n. 3, p. 031022, 2014.
- 5 PRAWER, S.; AHARONOVICH, I. **Quantum information processing with diamond**: principles and applications. Amsterdam: Elsevier, 2014.
- 6 BALASUBRAMANIAN, G. *et al.* Ultralong spin coherence time in isotopically engineered diamond. **Nature Materials**, Nature Publishing Group, v. 8, n. 5, p. 383–387, 2009.
- 7 DEGEN, C. Scanning magnetic field microscope with a diamond single-spin sensor. **Applied Physics Letters**, American Institute of Physics, v. 92, n. 24, p. 243111, 2008.
- 8 TAYLOR, J. *et al.* High-sensitivity diamond magnetometer with nanoscale resolution. **Nature Physics**, Nature Publishing Group, v. 4, n. 10, p. 810–816, 2008.
- 9 BALASUBRAMANIAN, G. *et al.* Nanoscale imaging magnetometry with diamond spins under ambient conditions. **Nature**, Nature Publishing Group, v. 455, n. 7213, p. 648–651, 2008.
- 10 MAZE, J. R. *et al.* Nanoscale magnetic sensing with an individual electronic spin in diamond. **Nature**, Nature Publishing Group, v. 455, n. 7213, p. 644–647, 2008.
- 11 MAERTZ, B. *et al.* Vector magnetic field microscopy using nitrogen vacancy centers in diamond. **Applied Physics Letters**, American Institute of Physics, v. 96, n. 9, p. 092504, 2010.
- 12 MCGUINNESS, L. P. *et al.* Quantum measurement and orientation tracking of fluorescent nanodiamonds inside living cells. **Nature Nanotechnology**, Nature Publishing Group, v. 6, n. 6, p. 358–363, 2011.

- 13 SCHIRHAGL, R. *et al.* Nitrogen-vacancy centers in diamond: nanoscale sensors for physics and biology. **Annual Review of Physical Chemistry**, Annual Reviews, v. 65, p. 83–105, 2014.
- 14 BALASUBRAMANIAN, G. *et al.* Nitrogen-vacancy color center in diamond—emerging nanoscale applications in bioimaging and biosensing. **Current Opinion in Chemical Biology**, Elsevier, v. 20, p. 69–77, 2014. DOI:10.1016/j.cbpa.2014.04.014.
- 15 LI, R. *et al.* Nanoscale electrometry based on a magnetic-field-resistant spin sensor. **Physical Review Letters**, APS, v. 124, n. 24, p. 247701, 2020.
- 16 DOLDE, F. *et al.* Electric-field sensing using single diamond spins. **Nature Physics**, Nature Publishing Group, v. 7, n. 6, p. 459–463, 2011.
- 17 CHEN, E. H. *et al.* High-sensitivity spin-based electrometry with an ensemble of nitrogen-vacancy centers in diamond. **Physical Review A**, APS, v. 95, n. 5, p. 053417, 2017.
- 18 ACOSTA, V. M. *et al.* Temperature dependence of the nitrogen-vacancy magnetic resonance in diamond. **Physical Review Letters**, APS, v. 104, n. 7, p. 070801, 2010.
- 19 CHOI, J. *et al.* Probing and manipulating embryogenesis via nanoscale thermometry and temperature control. **Proceedings of the National Academy of Sciences**, National Academy Sciences, v. 117, n. 26, p. 14636–14641, 2020.
- 20 NEUMANN, P. *et al.* High-precision nanoscale temperature sensing using single defects in diamond. **Nano Letters**, ACS Publications, v. 13, n. 6, p. 2738–2742, 2013.
- 21 BEVERATOS, A. *et al.* Single photon quantum cryptography. **Physical Review Letters**, APS, v. 89, n. 18, p. 187901, 2002.
- 22 ALLÉAUME, R. *et al.* Experimental open-air quantum key distribution with a single-photon source. **New Journal of Physics**, IOP Publishing, v. 6, n. 1, p. 92, 2004.
- 23 WALDHERR, G. *et al.* Violation of a temporal bell inequality for single spins in a diamond defect center. **Physical Review Letters**, APS, v. 107, n. 9, p. 090401, 2011.
- 24 HOWARD, M. *et al.* Quantum process tomography and linblad estimation of a solid-state qubit. **New Journal of Physics**, IOP Publishing, v. 8, n. 3, p. 33, 2006.
- 25 WALLRAFF, A. *et al.* Strong coupling of a single photon to a superconducting qubit using circuit quantum electrodynamics. **Nature**, Nature Publishing Group, v. 431, n. 7005, p. 162–167, 2004.

- 26 ZHANG, H. *et al.* Little bits of diamond: optically detected magnetic resonance of nitrogen-vacancy centers. **American Journal of Physics**, American Association of Physics Teachers, v. 86, n. 3, p. 225–236, 2018.
- 27 DAVIES, G.; HAMER, M. Optical studies of the 1.945 eV vibronic band in diamond. **Proceedings of the Royal Society of London A**, The Royal Society London, v. 348, n. 1653, p. 285–298, 1976.
- 28 DAVIES, G. Dynamic Jahn-Teller distortions at trigonal optical centres in diamond. **Journal of Physics C**, IOP Publishing, v. 12, n. 13, p. 2551, 1979.
- 29 PREEZ, L. D. **Electron paramagnetic resonance and optical investigations of defect centre in diamond**. 1965. 309 p. Thesis (Doctor in Philosophy) – University of Witwaters, Johannesburg, 1965.
- 30 LOUBSER, J.; WYK, J. van. Electron spin resonance in the study of diamond. **Reports on Progress in Physics**, IOP Publishing, v. 41, n. 8, p. 1201, 1978.
- 31 TOGAN, E. *et al.* Quantum entanglement between an optical photon and a solid-state spin qubit. **Nature**, Nature Publishing Group, v. 466, n. 7307, p. 730–734, 2010.
- 32 DOHERTY, M. W. *et al.* The negatively charged nitrogen-vacancy centre in diamond: the electronic solution. **New Journal of Physics**, IOP Publishing, v. 13, n. 2, p. 025019, 2011.
- 33 MANSON, N.; HARRISON, J.; SELLARS, M. Nitrogen-vacancy center in diamond: model of the electronic structure and associated dynamics. **Physical Review B**, APS, v. 74, n. 10, p. 104303, 2006.
- 34 MAZE, J. R. *et al.* Properties of nitrogen-vacancy centers in diamond: the group theoretic approach. **New Journal of Physics**, IOP Publishing, v. 13, n. 2, p. 025025, 2011.
- 35 GALI, A.; SIMON, T.; LOWTHER, J. An ab initio study of local vibration modes of the nitrogen-vacancy center in diamond. **New Journal of Physics**, IOP Publishing, v. 13, n. 2, p. 025016, 2011.
- 36 LARSSON, J.; DELANEY, P. Electronic structure of the nitrogen-vacancy center in diamond from first-principles theory. **Physical Review B**, APS, v. 77, n. 16, p. 165201, 2008.
- 37 DELANEY, P.; GREER, J. C.; LARSSON, J. A. Spin-polarization mechanisms of the nitrogen-vacancy center in diamond. **Nano Letters**, ACS Publications, v. 10, n. 2, p. 610–614, 2010.

- 38 GUGLER, J. *et al.* Ab initio calculation of the spin lattice relaxation time t_1 for nitrogen-vacancy centers in diamond. **Physical Review B**, APS, v. 98, n. 21, p. 214442, 2018.
- 39 STONEHAM, A. **Theory of defects in solids**: electronic structure of defects in insulators and semiconductors. Oxford: Clarendon Press, 1975.
- 40 STEINER, M. *et al.* Universal enhancement of the optical readout fidelity of single electron spins at nitrogen-vacancy centers in diamond. **Physical Review B**, APS, v. 81, n. 3, p. 035205, 2010.
- 41 DOLDE, F. **The nitrogen vacancy center in internal and external fields**. 2014. Thesis (Doctoral) – Universität Stuttgart, Stuttgart, 2014.
- 42 FELTON, S. *et al.* Hyperfine interaction in the ground state of the negatively charged nitrogen vacancy center in diamond. **Physical Review B**, APS, v. 79, n. 7, p. 075203, 2009.
- 43 ALBRECHT, A. **Controlled quantum dynamics of nitrogen vacancy centers in diamond**. 2015. Thesis (Doctoral) – University of Ulm, Ulm, 2015.
- 44 FUCHS, G. *et al.* Excited-state spectroscopy using single spin manipulation in diamond. **Physical Review Letters**, APS, v. 101, n. 11, p. 117601, 2008.
- 45 COLLINS, A.; THOMAZ, M.; JORGE, M. I. B. Luminescence decay time of the 1.945 eV centre in type Ib diamond. **Journal of Physics C**, IOP Publishing, v. 16, n. 11, p. 2177, 1983.
- 46 ACOSTA, V. M. *et al.* Diamonds with a high density of nitrogen-vacancy centers for magnetometry applications. **Physical Review B**, APS, v. 80, n. 11, p. 115202, 2009.
- 47 ROGERS, L. *et al.* Infrared emission of the NV centre in diamond: Zeeman and uniaxial stress studies. **New Journal of Physics**, IOP Publishing, v. 10, n. 10, p. 103024, 2008.
- 48 ACOSTA, V. *et al.* Optical properties of the nitrogen-vacancy singlet levels in diamond. **Physical Review B**, APS, v. 82, n. 20, p. 201202, 2010.
- 49 ABRAGAM, A.; BLEANEY, B. **Electron paramagnetic resonance of transition ions**. Oxford: OUP Oxford, 2012.
- 50 BAUCH, E. *et al.* Ultralong dephasing times in solid-state spin ensembles via quantum control. **Physical Review X**, APS, v. 8, n. 3, p. 031025, 2018.
- 51 HAHN, E. L. Spin echoes. **Physical Review**, APS, v. 80, n. 4, p. 580, 1950.

-
- 52 DIKANOVA, S. A.; TSVETKOV, Y. **Electron spin echo envelope modulation (ESEEM) spectroscopy**. Boca Raton: CRC press, 1992.
- 53 JARMOLA, A. *et al.* Temperature-and magnetic-field-dependent longitudinal spin relaxation in nitrogen-vacancy ensembles in diamond. **Physical Review Letters**, APS, v. 108, n. 19, p. 197601, 2012.
- 54 WALKER, M. A t5 spin-lattice relaxation rate for non-kramers ions. **Canadian Journal of Physics**, NRC Research Press Ottawa, v. 46, n. 11, p. 1347–1353, 1968.
- 55 REDMAN, D. *et al.* Spin dynamics and electronic states of n-v centers in diamond by epr and four-wave-mixing spectroscopy. **Physical Review Letters**, APS, v. 67, n. 24, p. 3420, 1991.
- 56 ASHCROFT, N. W.; MERMIN, N. D. **Solid state physics**. New York: Harcourt College Publishers, 1976. v. 1.