Development of a Diamond Defect Quantum Sensing Platform for Probing Novel Quantum Magnetic Phases

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Development of a Diamond Defect Quantum Sensing Platform for Probing Novel Quantum Magnetic Phases

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Abstract

Nitrogen vacancy centers in diamond are highly effective quantum sensors due to their high spatial resolution and high magnetic field sensitivity. We present the construction of an optically detected magnetic resonance platform in order to facilitate the probing of magnetic phases in two-dimensional heterostructures. This includes the characterization of the required microwave voltage controlled oscillator and amplifier. In the presence of crystal strain, we measure ensemble nitrogen vacancy spin transitions with and without an applied magnetic field, and observe frequency shifts consistent with sample heating.
I Introduction

Nitrogen vacancy (NV) centers in diamond are highly effective quantum sensors due to their high spatial resolution and high magnetic field sensitivity. A NV center is a defect within the carbon lattice of diamond formed by the substitution of a nitrogen atom and a neighboring lattice vacancy. When the defect is negatively charged, two paired electrons form a spin 1 system that is optically spin polarizable using a 532 nm laser. In addition, the spin state is optically detectable due to the higher probability of fluorescence for the $|m_s = 0\rangle$ state over the $|m_s = \pm 1\rangle$ states [1]. Through measuring the spin transitions, NV center spectroscopy provides a relatively cost effective and efficient probe into the magnetic field near the defect. By placing NV centers near two-dimensional heterostructures consisting of graphene, RuCl$_3$, and other materials and then performing optically detected magnetic resonance (ODMR) spectroscopy, we plan to probe novel quantum magnetic phases.

This thesis is organized as follows: In Section II, we will discuss the $C_{3v}$ symmetry within NV centers, the electron energy levels that result, and a model for the ground-state Hamiltonian. In Section III, various measurement protocols and the measurement apparatus for ensemble NV center measurements at room temperature are outlined. In Section IV, electron spin resonance spectra both with and without field and the effect of different laser power on NV center spectra are presented.

I.I Crystal Structure

The diamond lattice is a face-centered cubic Bravais lattice with a basis of two carbon atoms at each lattice site, and eight atoms per unit cell. The two atoms of a site are located at (000) and $(\frac{1}{4} \frac{1}{4} \frac{1}{4})$ in lattice coordinates. Each carbon has four nearest neighbors forming a tetrahedron shown in Fig: (2). The crystal can be constructed by defining a cube with vertices matching the tetrahedron and then stacking said cube with a (111) bond direction [2]. The crystal can also be viewed as two overlapping face-centered cubic lattices separated by $\frac{1}{4}$ lattice constant in each direction.
Figure 1. A carbon atom within the diamond lattice and its four bonds. By using the vertices to define a cube, the diamond crystal can be constructed by stacking with a (111) bond orientation.

Figure 2. A diamond unit cell. The red atoms are fully bonded within the unit cell. The black atoms are partially bonded within the unit cell. The green atoms are bonded solely outside the unit cell.

The NV center is formed by substituting a carbon atom for a nitrogen atom and another carbon atom for a vacancy within the lattice. NV centers occur naturally in diamond, but artificially enriched diamond can be prepared via nitrogen and helium ion implantation and annealing [3], or by incorporating the nitrogen during chemical vapor deposition, helium implantation to create vacancies, and annealing [4]. NV-center-enriched diamond can be synthesized as nanocrystals, thin films, or bulk crystals depending on the application. In the chemical vapor deposition method, the in situ doping of nitrogen should decrease broadening in the NV center spin transitions due to strain as discussed further in Section II.I. The crystal strain is reduced by avoiding non uniform-in-depth nitrogen incorporation and avoiding lattice damage caused by ion implantation. After implanting the grown diamond substrate with He+ ions, NV center density has been observed to increase by up to 60-fold over the non-implanted case [4].
II Electron Energy Levels

Figure 3. Excited and ground states for the spin 1 triplets and spin 0 singlets using the notation for the $C_3\nu$ symmetry group. Zero-phonon lines connect $^3A_2$ and $^3E$ while spin-orbit coupling induces triplet-singlet intersystem crossing between $^3E$ and $^1A_1$. Dashed lines represent non-radiative transitions [1].

A NV center, specifically the negatively charged NV$^-$ state, consists of six electrons [5]. Three are from the dangling bonds from carbon atoms near the vacancy. The two nitrogen valence electrons that are not covalently bounded to nearby carbons and one more electron from the negative charge state account for the rest of the six electrons. The two electrons not involved in lattice bonds form triplet and singlet states which can be shown by the tensor product of two spin $\frac{1}{2}$ doublets $\frac{1}{2} \otimes \frac{1}{2} = 1 \oplus 0$. In bra-ket notation, with states of the form $|s, m_s\rangle$, the triplet and singlet states correspond to $|1, 1\rangle$, $|1, 0\rangle$, $|1, -1\rangle$, and $|0, 0\rangle$ respectively.

While two other charge states exist, NV$^0$ and NV$^+$, neither state is magneto-optically active, and thus they are not useful for ODMR measurements. However, conversion of NV$^-$ near the diamond surface into NV$^0$ does pose a significant chal-
Figure 4. The symmetry elements of the $C_{3v}$ group shown on an equilateral triangle. In the absence of strain, NV centers exhibit $C_{3v}$ symmetry.

... challenging towards the generation of high concentrations of very shallow NV centers [5].

The NV center energy levels consist primarily of a ground state spin triplet denoted $^3A_2$, an excited spin triplet denoted $^3E$, and two singlet states denoted $^1A_1$ and $^1E$ [1]. The notation for the states reflects the $C_{3v}$ symmetry of a nitrogen vacancy. The $C_{3v}$ group contains the symmetry elements $E$, the identity, $C_3$, 120° rotational symmetry, and three $\sigma_v$ plane symmetries. An equilateral triangle is a simple shape that exhibits $C_{3v}$ symmetry as shown in Fig: (4). The NV center symmetry can be clearly seen in the tetrahedron of Fig: (2) when the central atom is replaced with a nitrogen and any of the other atoms are replaced with a vacancy.

II.I Ground-State Hamiltonian

The ground state triplet $^3A_2$ can be modelled by the Hamiltonian $H_{tot} = H_S + H_{SI} + H_I$ where the three terms refer to the electronic spin, hyperfine coupling to the nitrogen nucleus (I = 1), and nuclear portions respectively [1]. Each component is given by the following equations:

$$
\begin{align*}
H_S &= DS_z^2 + E(S_x^2 - S_y^2) + g_s \mu_B \vec{B} \cdot \vec{S} \\
H_{SI} &= A_\parallel S_z I_z + A_\perp (S_x I_x + S_y I_y) \\
H_I &= PI_z^2 - g_I \mu_N \vec{B} \cdot \vec{I}
\end{align*}
$$
<table>
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<th>Coefficient</th>
<th>Description</th>
<th>Value</th>
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<tr>
<td>E</td>
<td>Transverse Zero Field Splitting Parameter</td>
<td>kHz-MHz[1]</td>
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<td>$\mu_N$</td>
<td>Nuclear Magneton</td>
<td>$5.051 \times 10^{-27} J_T[6]$</td>
</tr>
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</table>

**Table 1:** Parameters for the $^3A_2$ Hamiltonian. E is non-zero in the presence of crystal strain. Units such that $\hbar=1$.

The $H_S$ component consists of an axial zero field splitting term, a transverse zero field splitting term, and an electron Zeeman effect term. The axial zero field splitting parameter D arises from electron dipole-dipole interactions while the transverse zero field splitting term is only non-zero in the presence of crystal strain.

The $H_{SI}$ component features an axial and transverse hyperfine coupling of the electron spins to the nitrogen nucleus. In addition, there are omitted terms originating from hyperfine coupling to $^{13}$C atoms. Due to this, it is beneficial to use isotopically purified $^{12}$C during the diamond growth process.

The $H_I$ component consists of a nuclear zero field splitting term analogous to the electron axial zero field splitting term and a nuclear Zeeman effect term.

Looking only at the electron spin portion $H_S$ and assuming $E=0$, the $|m_s = \pm 1\rangle$ states are degenerate in the absence of any magnetic field. When an arbitrary magnetic field is applied to an ensemble of NV centers, eight peaks are expected due to Zeeman splitting on the four possible orientations of the defects. In certain magnetic field directions, such as the (100) crystal orientation where the field is same for all
NV center orientation, only two peaks are expected.

When crystal strain is accounted for, the transverse zero field splitting parameter is non-zero and the $|m_s = \pm 1\rangle$ states are no longer degenerate for zero magnetic field. This can be attributed to the breaking of the $C_{3v}$ symmetry when strain is introduced. The number of expected peaks increases by a factor of two compared to the zero strain case. When measuring an ensemble of NV centers in material such as diamond dust, non-zero strain imposes a limit on the resolution of any spectrum as the ensemble will have a distribution of strains which widen the zero field peaks and any subsequent Zeeman splitting peaks.

In equilibrium, the sublevels of the ground state $^3A_2$ shown in Fig: (3) are almost uniformly populated. However, the system can be prepared into a spin polarized $|m_s = 0\rangle$ state by exciting the electron pair from the ground state into the $^3E$ levels using a 532 nm laser, because the $^3E |m_s = \pm 1\rangle$ states have a higher probability to undergo triplet-singlet intersystem crossing to the $^1A_1$ state. This then decays through either radiative or non-radiative transitions into the $^1E$ singlet and then into the $^3A_2 |m_s = 0\rangle$ state. Spin polarization into $|m_s = 0\rangle$ of up to 80% or more of the total population is possible [1]. The spin polarization is optically detectable due to the higher probability of fluorescence of red light for the $|m_s = 0\rangle$ state over the $|m_s = \pm 1\rangle$ states. This combination of optical spin polarizability and optical spin-state detectability is a key reason for the effectiveness of NV centers as quantum sensors.

### III Measurement

A basic measurement requires a laser to polarize spins, a microwave source to probe the spin resonances, and a light sensor to monitor the emitted light intensity. When the microwave source is resonant with a spin transition from $|m_s = 0\rangle$ to $|m_s = \pm 1\rangle$, the emitted red light will drop in intensity as spins transition from the baseline $|m_s = 0\rangle$ polarized state.
**Figure 5.** A key feature of NV centers is their optical spin polarization and their spin state dependent fluorescence. On the left, an ensemble of NV centers within diamond dust is illuminated with 532 nm light. On the right is a photograph from the same location, but through a red light bandpass filter showing the red light fluorescence when the system is polarized into a $|m_s = 0\rangle$ state.

**III.I Measurement Protocols**

A wide array of sensing protocols are viable with NV centers. In the simplest form of measurement, an ensemble of NV centers can be measured using a 532 nm laser, a light sensor, and a microwave source. The NV centers are continuously doped into a $|m_s = 0\rangle$ state while the microwave source is continuously swept with a sawtooth wave. An oscilloscope measuring both the sawtooth and light sensor output then records the electron spin resonance spectrum.

In order to increase the signal-to-noise ratio, pulsed measurements can also be implemented. The spin is first pumped into a $|m_s = 0\rangle$ state by a laser pulse and then free precession is induced by a $\pi/2$ pulse. After some time, the precession is halted by a second $\pi/2$ pulse, and then the spin state is read out by another pulse. After doing this many times and plotting intensity with respect to evolution time, there are oscillations in the intensity called Ramsey fringes which share a frequency with the electron spin resonance yielding an equivalent magnetic field value. This technique benefits from no optical pumping during the sensing period. Even higher frequency measurements can be performed using magnetic resonance relaxometry.
The $T_1$ relaxation time reflects the magnetic noise near the NV center at similar frequencies. This allows measurements of magnetic noise and does not require any microwave excitation [5].

One of the most promising applications of NV centers is their use as single spin quantum sensors for the measurement of magnetic phases on the atomic scale [5][7]. In a measurement akin to atomic force microscopy (AFM), a diamond AFM tip containing a single NV center is scanned across the sample surface. By interrogating the NV center with microwave frequencies, a spatial map of the magnetic field extremely close to the sample surface can be found.

![Figure 6. A simplified ensemble NV center measurement apparatus diagram.](image-url)
III.II Optical Apparatus

Within the apparatus, the optics begin with a 150 mW 532 nm laser (Compass 215m-15) which then optionally passes through a combination of neutral density filters (Thorlabs NE06A & NE10A) before a 532 nm laser line filter (Thorlabs FL532-10). The beam then reflects off of two mirrors on adjustable mounts with yaw and pitch degrees of freedom for beam steering. The beam then reflects off of a 550 nm cut-on dichroic mirror (Thorlabs DMLP550) before being focused onto a sample of NV center enriched diamond dust by a 10x objective. The chosen objective features a 1.7 cm working distance in order to accommodate future placement of the sample into a cryostat.

The emitted red light is collimated by the objective and then passes through the dichroic mirror, a 600 nm longpass filter (Thorlabs FEL0600), and a 750 nm shortpass filter (Thorlabs FES0750) before arriving at an adjustable gain Si photodetector (Thorlabs PDA36A2). Parts such as 1/2” optical posts (Thorlabs TR1), clamping forks (Thorlabs CF125), pedestal base adapters (Thorlabs BE1), 1” lens mounts (Thorlabs LMR1), and 1” lens tubes (Thorlabs SM1L03) were used throughout.

III.III Microwave Apparatus

A microwave sweep near 2.87 GHz is generated by supplying a sawtooth wave to a voltage controlled oscillator (VCO) (Mini-Circuits ZX95-3800ARS+) which then passes through a microwave amplifier (Mini-Circuits ZRL-3500+). Depending on antennae design, the microwave amplifier is not strictly necessary. The microwaves are conducted to the sample which sits atop a coplanar waveguide before terminating at a 50 \( \Omega \) impedance to ground.

The calibration curve shown in Fig: (7) is used to transform the recorded sawtooth wave into the corresponding wave across microwave frequencies for spectra.
Figure 7. VCO calibration curve as measured by a spectrum analyzer. The span of the spectrum analyzer was 5.946 MHz with a 30 KHz resolution bandwidth throughout. The microwave amplifier was also used during this measurement.

Table 2: Measured characteristics of the VCO and amplifier for a 5.495 V input (2.594 GHz output).
Figure 8. Bode plot for the Mini-Circuits ZRL-3500+ microwave amplifier.

This is done in Python using a univariate linear spline with a smoothing factor of $s=0.0001$. In order to ensure repeatable and standard use of the same VCO calibration curve, the spline was saved as a numpy object using the program shown in Code: (1) in Appendix: (A). This can then be loaded and used as the python module shown in Code: (2) in Appendix: (A). By placing this into a computer’s python module directory, a standard VCO calibration curve across experiments can be guaranteed.

The VCO and amplifier output a sharply defined peak as shown in Table: (2). For an output frequency of 2.594 GHz, the measured quality factor, defined by $Q = \frac{f_c}{\Delta f}$, is 67,000. While the change in amplifier gain across the microwave band seen in Fig: (8) is not trivial, it is not problematic due to the overall large microwave power (17.7 dBm at 2.594 GHz) and relatively small sweeping range (<300 MHz) during a typical measurement.
Figure 9. Ensemble measurement of NV center enriched diamond dust showing non-zero strain splitting. Using a 0.6 OD (25% transmission) neutral density filter. The vertical striping is due to limitations of the oscilloscope dynamic range and 8 bit ADC.

IV    Ambient NV Center Measurements

Once the VCO was calibrated, an oscilloscope was used to record both the light sensor signal output and the sawtooth wave input for the VCO in order to perform ODMR spectroscopy. In order to convert the recorded sawtooth wave to the corresponding microwave frequency sweep, the recorded wave was processed using the python program documented in Code: (2) in Appendix: (A). The split peaks at 2.874 GHz and 2.881 GHz in the zero field splitting shown in Fig: (9) are due to non-zero strain that is represented by E in the Hamiltonian discussed previously. The 7.2 MHz splitting represents the peak of the strain distribution of the ensemble NV centers. The average of the two peaks, 2.8775 GHz, agrees with the expected 2.87 GHz peak. The difference is most likely due to heating effects discussed below.
Figure 10. A NV center spectrum with a magnetic field applied via a permanent magnet. There are 16 peaks due to the four NV center alignments and strain induced splitting. No ND filters.

Figure 11. The same NV center spectrum as Fig. (10) but sweeping only the lower half. The eight spin transition peaks are shown with arrows. No ND filters.
When a magnetic field is applied, the $|m_s = \pm 1\rangle$ degeneracy is broken and Zeeman splitting occurs. In the absence of strain, this results in eight peaks; however with non-zero strain, there is an additional factor of two. The 16 peaks are observed as expected within Fig: (10) and Fig: (11). While the peak near 2.74 GHz in Fig: (11) is faint, the symmetric peak near 3.02 GHz lends further evidence. More precise spectra of the entire ODMR spectrum could not be taken due to measurement apparatus limitations. This could be improved relatively simply by switching to an oscilloscope with a 12 bit ADC and higher memory depth or recording direct measurements of the light sensor and function generator over time rather than recording an oscilloscope trace.

IV.I Laser Power Dependence

![NV Center Zero Field Splitting Laser Power Dependence](image)

**Figure 12.** When the laser power is reduced with a 0.6 OD (25% transmission) neutral density filter, the zero field splitting is shifted upward in frequency. This is consistent with a local temperature shift in the NV centers and is indicative of the laser heating the sample when at full power.

The zero field splitting spectrum was measured multiple times ($n=4$) with
no neutral density filters and with 0.6 OD neutral density (ND) filter in order to see the laser power dependence of the spectrum. One such measurement is shown in Fig: (12). The order of with or without a neutral density filter was varied, but consistently an increase in the frequency of the splitting was measured when the ND filter was used. This shift is consistent with the expected temperature dependence of the zero field splitting parameter $D$ [8]. Using $\frac{\partial D}{\partial T} = -74.2 \frac{kHz}{K}$ and assuming $D$ is linear with respect to temperature, the frequency shift would be equivalent to a $89K \pm 16K$ temperature shift if entirely explained by sample heating. This is plausible due to poor thermal coupling to the diamonds; however, alinearity in $D$ with respect to temperature will add additional error. This temperature shift persists in the presence of a magnetic field as shown in Fig: (13).

The variability of NV center resonances with temperature poses a significant challenge and source of error for room temperature measurements. One possible solution is to reduce temperatures; NV centers are significantly more stable with
respect to temperature changes in a cryogenic environment [9].

IV.II Laser Power Density

Currently, due to relatively large spot size, the sample receives a large overall power while receiving a relatively low laser power density. This is due to poor sample adjustment in the direction of the beam axis, and spot size increases due to diffraction. The sample adjustment can be trivially adjusted with an XYZ stage.

\[
\phi_{\text{Spot Size}} = \phi_{\text{Diffraction}} + \phi_{\text{Aberration}} = \frac{4\lambda M^2 f}{\pi D} + \frac{kD^3}{f^2}
\]  

(1)

Spot size is dictated by the Equation: (1) where \(\lambda\) is wavelength, \(f\) is the lens focal length, \(D\) is input beam diameter, \(k\) is the lens index of refraction, and \(M^2\) is the beam quality factor [10]. At small input beam diameters, the diffraction contribution dominates while at large input diameters spherical aberration dominates. In between by expanding the pre-objective beam using a beam expander, a minimal spot size can be achieved. The increased power density of a smaller spot size is proportional to the spin polarization and thus signal strength. In addition, it allows for decreases in overall laser power while maintaining signal strength.

V Conclusion

We have demonstrated successful measurement of the NV center spin transition spectrum with and without magnetic field. In addition, dependence on laser intensity consistent with the change in the zero field splitting with respect to temperature is observed. The next step will be the implementation of an XYZ sample stage, a beam expander, and subsequently measuring magnetic phases of two-dimensional heterostructures and taking measurements below ambient temperatures. Sub-ambient measurements will be possible once the sample stage is placed within a helium pulse tube cryostat. Significant headway has already been made including the construction
of a water cooling loop and mounting of the pulse tube. Sub-ambient measurements will also partially solve the issue of laser-sample heating due to decreased sensitivity to thermal change in the zero field splitting at low temperatures.

VI Acknowledgements

I would like to thank my research advisor Dr. Erik Henriksen, Yashika Kapoor, Jesse Balgley, Xinyi Du, and everyone else within the Henriksen lab group for technical advice throughout this project. I would also like to thank Joe Kitzman from Michigan State University for advice about optical component alignment and discussion of ODMR spectra. “Little bits of diamond: Optically detected magnetic resonance of nitrogen-vacancy centers” [11] was used as a basis for the optical design.

References


A Appendix

import numpy as np
import pandas as pd
import scipy.interpolate as interp

dfPath = "VCO_voltage_vs_frequency_curve.csv"
columnNames = ["Voltage", "Frequency"]
df = pd.read_csv(dfPath, header=0, names=columnNames)
calibrationData = np.concatenate(([df[columnNames[0]].to_numpy()]),
                                 [df[columnNames[1]].to_numpy()]), axis=0)
interpolatedVCOCurve = interp.UnivariateSpline(calibrationData[0],
                                                calibrationData[1], s=0.0001, k=1)
np.save("./VCO_interpolated_spline_object", interpolatedVCOCurve,
        allow_pickle=True)

Code 1: Python code in order to generate and save the VCO calibration curve.

from os import path
import numpy as np

resources_dir = path.join(path.dirname(__file__), 'resources')
splinePath = resources_dir+"/VCO_interpolated_spline_object.npy"
interpolatedCurve = np.load(splinePath, allow_pickle=True)[()]

def voltageToFrequency(voltage):
    microwaveFrequency = interpolatedCurve(voltage)
    return microwaveFrequency

Code 2: A python module that loads a univariate spline from a numpy object and
provides a function for converting a VCO input voltage to a microwave frequency.