The mechanical and thermal properties of the nitrogen-vacancy centre in diamond

A thesis submitted for the degree of
Doctor of Philosophy of
The Australian National University

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Declaration

This thesis is an account of research undertaken between February 2013 and December 2017 at the Laser Physics Centre, Research School of Physics and Engineering, The Australian National University, Canberra, Australia.

Except where acknowledged in the customary manner, the material presented in this thesis is, to the best of my knowledge, original and has not been submitted in whole or in part for a degree in any university.

______________________________
Michael Samuel James Barson
November 2018
for Sam
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Quantum technologies offer revolutionary new ways to perform metrology and process information. However, successfully exploiting quantum devices for new practical technology is a challenging problem. Due to the fragile nature of quantum states, precision measurements and operations using quantum objects are often confined to systems that are well protected from their environment. This can limit the practical use of such quantum devices. A quantum tool that can successfully and simply operate in ambient conditions would provide major advances in quantum technology.

In the past decade or so, the nitrogen-vacancy (NV) centre in diamond has proven itself to be a remarkably powerful tool for nanoscale quantum sensing and quantum information processing in ambient conditions. Despite these achievements, there are still several fundamental features of the NV centre which are not completely understood. This thesis addresses these areas in two parts, firstly the mechanical properties and secondly the thermal properties of the NV centre.

The effect of crystal stress or strain on the spin resonances on the NV centre ground state is theoretically described and then experimentally characterised; correcting previously contradictory attempts to explain the observed behaviour. The utility of this knowledge is demonstrated by force sensing in a microscopic diamond cantilever using a single NV centre. New unique concepts of force sensing and metrology based on the NV spin-mechanical interaction are explored.

The thermal properties of the NV centre's optical and spin resonances are theoretically described and experimentally characterised; providing the first successful description that details the origin of the effect of temperature on the spin resonance. Furthermore, the atomscopic changes in the NV centre's electronic orbitals due to the effect of crystal distortion are directly probed.

This complete understanding of the NV centre's mechanical and thermal behaviour enables metrology that spans the full magnetic-temperature-pressure range of the NV centre. For example, this is ideally suited to studying superconducting phase changes in high-pressure materials. A proof of principle measurement of phase changes in superconductors is demonstrated and new magnetic-temperature-
pressure metrology devices are discussed.

Magnetic circular dichroism (MCD) spectroscopy measurements are used to unpick some of the remaining mysteries of the NV centre. The magnetic structure of the singlet levels are directly measured for the first time and a large quenching of orbital angular momentum is observed. This provides further evidence of a Jahn-Teller interaction and its role in the lower inter-system crossing. These MCD observations greatly enhance the knowledge of the poorly understood, but critically important lower inter-system crossing.

Using MCD the fine-structure of the NV\(^0\) ground and excited states are measured for the first time and the reasons of their absence from previous measurements are discussed. The observation of the fine structure of NV\(^0\) ground state has been a long-standing mystery of the NV centre, this information will enable the pursuit of new applications of the NV centre that also incorporate NV\(^0\).
List of Papers

Publications relating to the content in this thesis


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CHAPTER 1

Introduction

1.1 Motivation

Quantum technologies by their very nature will provide the practical means to measure and simulate phenomena inaccessible to classical technology. Quantum computers promise fundamentally more powerful abilities to solve certain computational problems by exploiting uniquely quantum properties such as entanglement and superposition. Similarly, quantum sensing and microscopy can exploit the quantum properties and the atomic size of quantum probes to provide better sensitivity and resolution than their classical counterparts.

A challenging consequence of utilising quantum objects for computers or sensors is that often their quantum state is fragile or hard to read and control. Because of this fragility, many systems rely on isolation from their environment by using ultra-high vacuums (e.g. magnetic resonance force microscopy [1], scanning tunnelling microscopy [2]), cryogenic temperatures (e.g. SQUIDS [3], quantum dots [4], phosphorus in silicon [5], superconducting circuits [6]) or other sophisticated isolation devices (e.g. ion traps [7], magneto-optical traps [8]). This is particularly problematic for quantum sensors, as non-ambient conditions exclude many systems of critical interest in chemical and biomedical research, such as live specimens or highly temperature dependent proteins and molecules. A quantum system that is robust enough to be useful in ambient conditions is going to be a more capable sensor to study these important systems. Similarly, a quantum system that is small (atom-like) will have a natural ability to measure and image processes at length scales much smaller than larger and more isolated devices.

A quantum computer that can function at ambient conditions may be, in principle, scaled more simply. Even if only a small scale system is available in ambient conditions, it will make a useful and more accessible system to test and develop
quantum information processing (QIP) concepts more cheaply than a larger and more complex quantum computer.

Undoubtedly the most promising quantum system for use in ambient conditions is the atom-like nitrogen-vacancy (NV) centre in diamond. The NV centre has recently shown the ability to perform significant nano-metrology and microscopy feats. The detection of nuclear magnetic resonance (NMR) signals from single proteins has been demonstrated [9]. Further more, the NMR signal from very small volumes of nuclear spins has also been spatially imaged [10, 11, 12]. The electron spin resonance (ESR) signal from single electron spins has been imaged [13]. The invention of diamond scanning probes designed in the style of atomic force microscope (AFM) probes have been used for magnetic imaging with spatial resolution far beyond the diffraction limit [14, 15]. NV centres have been used to locate and measure single elementary charges [16] and single nuclear spins [17] at ambient conditions. This list of achievements is a testament to the NV centre’s variety of capabilities and its potential as a sensitive and versatile nano-scale metrology tool in ambient conditions.

Significant QIP achievements have also been demonstrated using NV centres. This includes quantum error correction [18], quantum registers [19, 20, 21], entanglement between photons and spins [22], loop-hole free entanglement between distant NV spins [23], and quantum memories [24, 25, 26]. Most of these QIP demonstrations are based on the concept of the spin-cluster, where an NV centre is surrounded by a group of nuclear spins such as $^{13}$C isotopic impurities and the intrinsic N nuclear spin. The nuclear spins are read out and controlled by the NV spin via hyperfine interactions; allowing for quantum information to be swapped between the nuclear and electronic spins. Such systems are experimentally much simpler than competing devices with similar capabilities, such as ion-traps [7] or phosphorus atoms in silicon [5].

As shown in figure 1.1, the interest in the NV centre is intense. This is essentially due to the potential for the NV to be a practical quantum tool for sensing and quantum information. However, there are still significant gaps in the understanding of the NV centre’s fundamental behaviour. In particular, the mechanical and thermal interactions of the NV centre are not as well documented or understood. Sensitive thermal studies and measurements using the NV centre have been demonstrated [27, 28, 29, 30, 31]. However, the underlying mechanism for the NV centre’s temperature behaviour has not been understood. Similarly, there have been demonstrations of the mechanical interaction of the NV centre, but with incomplete understanding of the interaction and no mention of the possibilities of spin-mechanical metrology [32, 33, 34, 35, 36, 37, 38].
1.1. MOTIVATION

Figure 1.1: Number of publications per year studying nitrogen-vacancy centres, data taken from the Web of Science using the topic keyword nitrogen-vacancy. https://webofknowledge.com

More information about the NV centre’s thermal and mechanical properties is also important for QIP applications. For a quantum computer to robustly operate in ambient conditions the influence of thermal and mechanical environmental factors on the quantum system must be thoroughly understood. This could be to limit the detrimental effects of fluctuations of the spin resonances during quantum gate operations from temperature or crystal stress changes, or dephasing from phonons. These interactions can also be beneficial, they can be used as an extra level of control on the NV spin and optical resonances, either by spin-mechanical mediated interactions or temperature tuning of resonances.

Absolutely critical to the NV centre’s success as a quantum tool is its spin-polarisation and spin read-out mechanisms. Since spin-polarisation and read-out underpin virtually every practical application of the NV centre’s use in quantum technology, it is worthwhile to fully investigate and understand these processes and their effect on the NV centre’s performance. The spin-polarisation and read-out properties both rely on inter-system crossings (ISC) between the spin triplet and spin singlet states. There are still fundamental deficiencies in the understanding of how these singlet states behave and the mechanisms of the ISCs. This is because there are relatively few direct observations of the NV singlet states using a limited variety of techniques. However, it is clear that vibrational effects play a strong role in the ISCs, as such, these processes are naturally investigated by mechanical and
CHAPTER 1. INTRODUCTION

thermal studies.

There are similar properties shared between the singlet states and the neutral charge NV centre (NV$^0$). Similar to the singlet states, relatively little is known about the NV$^0$ charge state. Despite attempts, no fine structure of NV$^0$ ground state has been observed. Due to the similarities with the singlet levels and the other applications that can utilise NV$^0$ (e.g. enhanced quantum memories [39] and electrical state read-out [40]), it is worthwhile to fully understand its fundamental structure.

An investigation that has not been pursued with the singlet states or NV$^0$ is magnetic circular dichroism (MCD) spectroscopy. MCD is an optical spectroscopy technique performed in large magnetic fields at low temperatures. It is sensitive to the magnetic fine structure of the levels between optically allowed transitions. The optical resonances of NV$^0$ and NV$^-$ singlet levels are both well known but their magnetic fine structure is not. As such, utilising MCD spectroscopy techniques is an obvious approach to learn more about the singlet levels and NV$^0$.

With full knowledge of the mechanical and thermal properties of the NV centre, applications over broad stress and temperature ranges can easily be pursued. For example magnetometry can be performed over a large temperature range and the unwanted temperature shifts factored out of the result. Similarly, NV centres can be implemented in high stress diamond applications if the stress dependence of the NV centre is understood. One obvious extension of these ideas is to use NV centres within a diamond anvil cell (DAC) and perform nanoscopic NV based metrology on high pressure samples over a wide temperature range. Such a device will prove invaluable in the pursuit of discovering new materials that form at high pressure.

1.2 Thesis overview

The aim of this thesis is to investigate the mechanical and thermal interactions of the NV centre to improve the understanding of the NV centre’s properties and their potential applications.

To address this aim, this thesis is divided into two parts. Firstly, the spin-mechanical interaction of the NV centre is defined, characterised, measured and examples of its application to novel spin-mechanical metrology detailed. The second part details the temperature behaviour of the NV centre resonances theoretically, then measures and characterises their effect experimentally. The remaining mysteries of the NV centre regarding the lower ISC, spin singlet states and the neutral charge state fine structure are investigated using MCD measurements. Finally, using
1.2. THESIS OVERVIEW

information from the temperature and mechanical characterisations, measurements of phase transitions in superconducting materials are demonstrated and discussed and a new experimental device for material science described.
CHAPTER 2

Literature review

2.1 Introducing the nitrogen-vacancy (NV) centre

2.1.1 Intrinsic properties

Before introducing the nitrogen-vacancy (NV) centre some remarks on the properties of diamond are worthwhile as it is a remarkable material. The strong covalently bonded carbon in diamond make the crystal very stiff causing it to be the hardest and most thermally conductive natural material. Diamond’s rigid crystal lattice also makes the crystal very stiff with an extremely high Young’s modulus ($\gtrsim 1000$ GPa). This allows for very high quality single crystal mechanical resonators [41, 42]. Diamond has a very large band gap of 5.5 eV (225 nm) making it transparent into the ultra-violet (UV). Diamond also has a relatively high refractive index of 2.42, a property exploited in its gemstone applications. Very pure diamond can be manufactured and the impurities can be controlled to be < 1 ppb. The most common impurities are nitrogen and boron, which give diamond a yellow and green colour respectively. Diamond is most commonly manufactured using chemical vapour deposition (CVD) or by high-pressure, high-temperature (HPHT) growth.

There are hundreds of documented colour centres in diamond [43] but the NV centre is the most famous. This is due to the NV centre’s unique and useful properties which offer enticing possibilities for quantum technologies that can take advantage of them. The following is a timeline of some of the major results concerning the NV centre in diamond.

- The first measurements of the NV centre were optical luminescence measurements by Du Preez in 1965 [44].
- The first mention of the nitrogen and vacancy structure was by Davies and Hamer in 1976 [45], they speculated this from the symmetry of the defect
determined by uniaxial stress and outlined the defect’s optical properties.

- The next major milestone was the measurement of the spin fine-structure, optical spin-polarisation and a proposal of the $^3A_2$ spin Hamiltonian by Loubser and Van Wyk in 1977 [46] using conventional EPR with optical pumping.

- In 1987 Reddy et al [47] used laser hole-burning and MCD experiments to determine the $^3A_2$ was the ground state of the NV$^-$ optical transition.

- In 1988 Van Oort et al [48] demonstrated optically detected magnetic resonance (ODMR) the NV$^-$ ground state spin.

- In 1995 Mita [49] determined that NV$^0$ and NV$^-$ were different charge states of the same defect.

- In 1997 Gruber et al [50] measured single NV centres and ODMR using scanning confocal microscopy, this achievement is the turning point for far more interest in the NV$^-$ centre.

- In 2004 Jelezko et al demonstrated coherent oscillations of a single NV$^-$ electron spin [51] and a single coupled $^{13}$C nuclear spin [17].

- In 2006 Manson et al [52] proposed a model for the spin-polarisation processes, inter-system crossing and state ordering of the NV$^-$ centre.

- In 2008 Taylor et al [53], Maze et al [54] and Balasubramanian et al [55] demonstrated nanoscale magnetometry using ODMR with single NV centres.

- In 2008 Rogers et al [56] observed the emission of the infra-red ZPL associated with the singlet levels.

- In 2006 Dutt et al [21] and in 2008 Neumann et al [19] demonstrated a spin-cluster, with high-fidelity entanglement of several nuclear spins around a single NV$^-$ centre.

- In 2016 Hensen et al [23] demonstrated the entanglement of two NV centres separated by 1.3 kms.

The large and disparate collection of works surrounding the NV centre prompted Doherty et al [57] to compile a review article in 2013 that details the entire history and accumulated knowledge of the NV centre up until that point. This in itself is a milestone, as it filled a need identified by the now very large community of researchers who wished to learn about the NV centre.

The NV centre in diamond consists of a single substitutional nitrogen impurity in place of a carbon atom and a vacancy (an empty lattice site) next to the nitrogen
impurity. The centre’s N-V axis is aligned along one of the four ⟨111⟩ crystallo-
graphic directions. The centre and has trigonal $C_{3v}$ symmetry, consisting of three
fold rotations about the ⟨111⟩ symmetry axis.

NV centres exist naturally in diamond but are more routinely engineered in
synthetic diamond. NV centres can be generated in high density in nitrogen rich
diamond if vacancies are provided. Vacancies can be created using particle irradi-
ation. The vacancies become mobile during annealing at temperatures above 600
°C and can localise at nitrogen sites creating NV centres [45]. NV centres can also
be created by ion implantation. The ions create damage and vacancies that are
localised to the implantation site. This allows for isolated NV centres to be made
in ultra-pure low nitrogen diamond (< 5 ppb) [58]. NV centres can also be formed
during CVD growth [59].

The electronic structure of the NV centre is due to the dangling bonds of the
carbon and nitrogen atoms around the vacancy. These bonds provide 5 electrons
to the defect for the neutral charged case NV$^0$. This thesis (apart from chapter
9) focuses on the negatively charged NV$^-$ defect, which gains an extra electron
(total of 6) from a donor somewhere in the diamond lattice. The stable charge
state of the NV centre is determined from the available surrounding electron donors
(predominately nitrogen). However, photo-ionisation can drive the centre between
the two charge states [60, 61, 62].

The electronic structure of the NV$^-$ and NV$^0$ charge states are shown in figure
2.1. The optical transition between the ground and excited triplets ($^3A_2$ and $^3E$)
of NV$^-$ are separated by a zero-phonon line (ZPL) of 637 nm (1.945 eV) [63]. The
metastable singlet states ($^1A_1$ and $^1E$) of NV$^-$ are separated by a ZPL of 1040

![Figure 2.1: (a) Electronic levels of the NV$^-$ centre. (b) Electronic levels of the
NV$^0$ centre.](image-url)
2.1. INTRODUCING THE NITROGEN-VACANCY (NV) CENTRE

nm (1.190 eV) [56, 64]. The NV\(^0\) ground and excited doublets (\(^2A_2\) and \(^2E\)) are separated by a 575 nm (2.156 eV) ZPL [65].

A broad phonon sideband extends beyond the zero-phonon line for NV\(^-\) with only \(~\frac{1}{4}\)% of the emission within the ZPL at room temperature. The phonon sideband is due to the overlap of exciting vibrational modes when transitioning between the ground and excited electronic states. For linear phonon coupling the vibrational potentials in the excited and ground electronic states are identical, as shown in figure 2.2(b). These identical potentials give emission and absorption phonon sidebands which are mirror images of each other. Small deviations from this mirror symmetry are often observed and due to quadratic electron-phonon coupling or Jahn-Teller interactions.

Practically, the absorption and emission sidebands allow for off-resonant excitation, usually with a 532 nm (2.331 eV) laser near the peak of the absorption band and detection in the fluorescence band which extends from 637 nm (1.945 eV) to 1000 nm (1.240 eV), as shown in figure 2.2(a). NV\(^0\) has similar absorption and emissions bands to the NV\(^-\) with a phonon sideband that extends up to the NV\(^-\) ZPL and can also be excited using 532 nm light. A sharp infra-red (IR) ZPL at 1040 nm (1.190 eV) between the metastable singlet states is also observable when the 637 nm transition is cycled [56, 66]. Curiously, in absorption [67] the phonon sideband of the IR ZPL is dramatically different to the emission phonon sideband. This is a largely unresolved mystery that accompanies other unexplained behaviour of the singlet states. It is expected that undetermined vibrational physics occurring in the singlet states is responsible for this behaviour. This is further discussed in later sections.

Relaxation from the excited state triplet to the ground state triplet occurs at a rate of 83 MHz (1/(12 ns) lifetime [68]). Unlike many fluorescent dyes or quantum dots, the centre doesn’t show blinking or bleaching (except for \(\lesssim\) 5 nm nanodiamonds [69]). This photo-stability enables continual monitoring of the NV\(^-\) centre. Photo-stability is also useful for continually tracking the centre spatially. The fluorescence is bright enough to resolve single emitting NV centres using high-resolution confocal microscopy [50, 70, 71]. Due to multi-directional emission and high refractive index of diamond causing internal reflections, the experimental photon count rate from a single NV\(^-\) in bulk diamond using conventional optics is about 300-400 kHz, less than 1% of all emitted fluorescence.

As shown in figure 2.3, NV\(^0\) has a comparable optical emission spectra [60] to NV\(^-\). NV\(^0\) also has a similar lifetime of \(~\frac{1}{4}\)9 ns [72] and single emitting centres have been observed [73]. As NV\(^0\) has 5 electrons it is expected to have a spin \(S = \frac{1}{2}\)
Figure 2.2: (a) Absorption and emission of the visible ZPL at low temperature ($\approx 60$ K), same sample used for uniaxial measurements in chapter 4. Approximate background nitrogen absorption is represented by the dashed line. (b) Depiction of absorption and emission between the ground and excited vibronic states, in this case an energy two phonons higher than the ZPL is absorbed (green), and the corresponding emission (red) two phonons lower in energy than the ZPL is emitted. The total phonon sidebands in (a) is a combination of many of these vibronic transitions. The axis $Q_i$ is the normal nuclear displacement corresponding to that phonon mode. The vibration potentials here are depicted as harmonic oscillators.
Figure 2.3: Emission spectra of NV\(^-\) (upper) and NV\(^0\) (lower) from ensemble measurements using 532 excitation. These spectra are taken from separate samples in which each shows much more emission of one charge state over the other. As indicated by the arrows there is a small but visible amount NV\(^0\) ZPL in the NV\(^-\) spectra and vice-versa.
CHAPTER 2. LITERATURE REVIEW

ground state. Mysteriously, no ground state spin resonances have been detected. Although, there has been a $S = \frac{3}{2}$ spin-polarised EPR signal detected in the quartet $^4A_2$ [74] level. Also, NMR signals have been assigned to the NV$^0$ ground state using photoionsiation experiments involving NV$^-$ [61]. Due to the absence of observations of spin resonances, comparatively little is known about NV$^0$.

For the NV$^-$ centre, the even number of six electrons create an integer spin system [75]. The $S = 1$ spin of the NV$^-$ centre has ground ($^3A_2$) and excited ($^3E$) state spin-triplets, which have a zero-field magnetic resonances at 2.88 GHz and 1.42 GHz respectively. The ground state splitting between the $m_s = 0$ and $m_s = \pm 1$ states was first detected by electron paramagnetic resonance (EPR) under optical illumination [46, 76]. However, today this is most commonly detected using optically detected magnetic resonance (ODMR) techniques [48].

ODMR is possible thanks to the inter-system crossings (ISC) to the meta-stable singlet states ($^1A_1$, $^1E$) from the $^3E$ level. As shown in figure 2.4, the non-radiative decay from the $^3E$ to the $^1A_1$ is slower for the $m_s = 0$ than for the $m_s = \pm 1$ spin projections. The non-radiative ISC transitions compete with the radiative decay, as such, the slower $m_s = 0$ upper ISC, makes the $m_s = 0$ spin projection brighter. After a few optical cycles the spin appears polarised into the bright $m_s = 0$ spin projection. This is also because the decay from the $^3E$ to the singlet states is stronger for $m_s = \pm 1$ spin projection and the decay out of the $^1E$ to the $^3A_2$ doesn’t further alter the spin-polarisation. Spin-polarisation [77] and ODMR are seen in other solid-state systems [78, 79, 80] and are usually a consequence of spin-orbit interactions. The NV$^-$ upper ISC which is primarily responsible for spin-polarisation and read-out has also been shown to be mediated by spin-orbit and vibronic interactions in the $^3E$ and the $^1A_1$ levels [81, 82]. However for the lower ISC, only the net rate out of the $^1E$ is known and not the relative amounts to the $m_s = 0$ or $m_s = \pm 1$ states [83]. Additionally, the fundamental mechanism of the lower ISC is not known at all.

The NV$^-$ spin, has the longest ever observed room temperature electron spin coherence time of $T_2 \sim 1.8$ ms (for isotopically pure diamond [84]). This is due to the low number of paramagnetic impurities that can be achieved in diamond, which provides a magnetic noise free environment to host the electron spin. For isotopically pure diamond, the $T_2$ dephasing is limited only by the spin-lattice relaxation time $T_1$ at room temperature.

Dephasing times in the order of $T_2 \sim 10 \leftrightarrow 100\mu s$ are more usual for common non-isotopically pure diamond. In this case the limiting factor is magnetic noise from impurities within the diamond lattice, predominately $^{13}$C nuclear spins. The dephasing effect of this magnetic noise is much larger than spin-phonon interactions.
2.1. INTRODUCING THE NITROGEN-VACANCY (NV) CENTRE

![Diagram of energy levels and transitions for the NV centre.]

**Figure 2.4:** The relative decay strengths for the inter-system crossing. Radiative and non-radiative transitions are denoted by solid and dashed arrows respectively.

as the spin-lattice relaxation time in diamond at room temperature is $T_1 \lesssim 4\,\text{ms}$ [85], much longer than the observed $T_2$. For NV centres close to the surface, $T_2$ can be shortened due to magnetic or electrical noises at the surface of the diamond [86, 87]. Engineering NV centres close to the surface with good spin coherence properties is an area of ongoing investigation [9, 88, 89, 90]. This is important as NV$^-$ centres with good coherence times and stability near to the surface are useful for sensing of phenomena outside of the diamond and close to the diamond surface.

Long spin coherence times are critical for the NV centre’s success as a practical quantum tool. A long spin-coherence time results in a spectrally narrower spin resonance. This sharper resonance allows for better sensitivity as smaller changes in spin resonance frequency can be detected. Alternatively, this can be understood as more time spent coherently sampling a signal prior to dephasing, resulting in better sensitivity and frequency resolution. Similarly, a long spin coherence time allows for more quantum operations to be performed before dephasing, a key metric for performance in quantum computing.

The coherence time in pure diamond is ultimately $T_1$ limited which is in turn limited by spin-phonon interactions. As such, it is worthwhile to investigate the spin-phonon interaction to better understand this limitation. The spin-phonon interaction is naturally investigated by performing thermal and mechanical experimental studies of the NV centre. This is because phonon populations are strongly temperature dependent and the coupling of phonons to the spin is mediated by the
CHAPTER 2. LITERATURE REVIEW

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Abundance</th>
<th>Nuclear Spin I</th>
<th>$A_\parallel$ (MHz)</th>
<th>$A_\perp$ (MHz)</th>
<th>$P$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{13}$C [46, 74]</td>
<td>1.1%</td>
<td>1/2</td>
<td>198.2(3)$^\dagger$</td>
<td>120.8(2)$^\dagger$</td>
<td>-</td>
</tr>
<tr>
<td>$^{14}$N [74, 91]</td>
<td>99.63%</td>
<td>1</td>
<td>-2.70(7)</td>
<td>-2.14(7)</td>
<td>-5.01(6)</td>
</tr>
<tr>
<td>$^{15}$N [74]</td>
<td>0.37%</td>
<td>1/2</td>
<td>3.65(3)</td>
<td>3.03(3)</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2.1: Hyperfine parameters of NV$^-$ ground state spin for nearby nuclear spins. $^{13}$C and $^{15}$N have no quadrupole moment. The $^{13}$C parameters shown are for the nearest carbon position only. Parameters for further carbon sites are available in the literature [74, 92]. † for $^{13}$C the axial component $A_\parallel$ is defined along a $\langle 111 \rangle$ which is not the symmetry axis of the NV centre i.e. at an angle $\theta = 109.5^\circ$, the angle between possible $\langle 111 \rangle$ directions.

the same spin-mechanical interaction of strain/stress in the crystal.

The ground state spin triplet can be described by the Hamiltonian [57],

$$H = D \left( S_z^2 - S(S + 1)/3 \right) + A_\parallel S_z I_z + A_\perp (S_x I_x + S_y I_y) + P \left( I_z^2 + I(I + 1)/3 \right),$$

(2.1)

where $D$ is the 2.87 GHz crystal field (or zero magnetic field) splitting; $A_\parallel$ and $A_\perp$ are the axial and non-axial hyperfine interaction terms and $P$ is the nuclear quadrupole term; and $S_x$, $S_y$, $S_z$ are the $S = 1$ spin matrices where $x, y, z$ are orientated in the NV coordinate system as shown in figure 2.5. $I_x$, $I_y$ and $I_z$ are the nuclear spin operators. The hyperfine interactions due to nearby nuclear spins are given in table 2.1.

In the presence of applied magnetic fields, electric field or stress/strain the following interaction is added,

$$V = \mu_B g_\parallel S_z B_z + \mu_B g_\perp (S_z B_x + S_y B_y)$$

$$+ \mu_N g_N \vec{I} \cdot \vec{B} + (d_\parallel E_z + M_z + D(T)) \left( S_z^2 - S(S + 1)/3 \right)$$

$$+ (d_\perp E_x + M_x) \left( S_y^2 - S_z^2 \right) + (d_\perp E_y + M_y) (S_x S_y + S_y S_x),$$

(2.2)

where $\mu_B$ (13.996 GHz/T) and $\mu_N$ (7.623 MHz/T) are the Bohr and nuclear magnetons; $g_\parallel$ and $g_\perp$ are the axial and transverse electronic $g$–factors and $g_N$ is the nuclear $g$–factor; $d_\parallel$ and $d_\perp$ are the axial and transverse electric field susceptibilities; $D(T)$ is the temperature dependent shift of the spin resonance $D$; $M_x, M_y, M_z$ are the $x, y, z$ interactions due to crystal stress/strain and have not been defined before this work and are explained in detail in part I; $\vec{B}$ and $\vec{E}$ are the applied magnetic and electric fields. The values of the relevant parameters are listed in table 2.2.
2.1. INTRODUCING THE NITROGEN-VACANCY (NV) CENTRE

\[ \omega \text{ (MHz)} \]

\[ 0 \text{ G} \]

\[ 20 \text{ G} \]

\[ 38 \text{ G} \]

\[ \omega \text{ (MHz)} \]

\[ 1.945 \text{ eV} \]

\[ 637 \text{ nm} \]

\[ 1.42 \text{ GHz} \]

\[ 2.87 \text{ GHz} \]

\[ \Delta \]

\[ \delta \]

\[ \text{ODMR spectra from an NV}^- \text{ ensemble for increasing magnetic field.} \]

\[ \text{Figure 2.5: (a) NV centre with crystal frame coordinate system X, Y, Z and the NV frame coordinate system x, y, z. The green N signifies the nitrogen and the pink V signifies the vacancy. Convention for trigonal symmetry requires the z axis be along the defect rotational axis (N-V direction), the x axis lie within a reflection plane of the defect (towards a carbon) and the y axis orthogonal to the other two axes. In this case z } \parallel \text{ [111], x } \parallel \text{ [112] and y } \parallel \text{ [110]. (b) The room temperature states of the fine structure of the NV}^- \text{ centre. The ground state splitting } (\Delta) \text{ of the degenerate spin states } (m_s = \pm 1) \text{ is caused by magnetic fields and non-axial components of strain or electric fields. The ground state shift } (\delta) \text{ of the spin resonances mean energy is caused by the axial components of strain or electric fields.} \]
Table 2.2: Susceptibility parameters for interactions with magnetic fields and electric fields for the NV\textsuperscript{−} ground state spin. If uncertainties are not shown they are much less than the displayed number of significant figures.

| $g_{||}$ \cite{74} | $g_{\perp}$ \cite{74} | $g_{N}$ \cite{93} | $d_{||}$ (Hz cm/V) \cite{94} | $d_{\perp}$ (Hz cm/V) \cite{94} |
|-------------------|-------------------|-------------------|-------------------|-------------------|
| 2.0029(2)         | 2.0031(2)         | 0.4038 \cite{14N} | -0.5664 \cite{15N} | 1.4048 \cite{13C} |
|                   |                   | 0.35(2)           |                   | 17.3(3)           |

2.1.2 ODMR and experimental techniques

Measurement of the ODMR spectra is usually performed by applying microwaves directly to the sample and monitoring the fluorescence from optical excitation. In simple constant-wave (CW) ODMR measurements, a laser is continuously exciting the NV\textsuperscript{−} and microwaves are swept through the resonant frequency. On resonance the microwaves change the state from $m_s = 0$ to the $m_s = \pm 1$ which is less bright and a dip in fluorescence is observed, as shown in figure 2.5(c). However, since the microwaves are fighting against the spin-polarising effect of the laser, powerful microwaves are needed which can result in power broadening of the resulting spin resonance spectra. The effect of power broadening can be seen in figure 2.6; as microwave power is increased the visibility of the $^{14}$N hyperfine peaks is lost. As previously mentioned, broad resonances are not desired for sensitive metrology. Pulsed measurements are advantageous as they use microwaves to drive the NV\textsuperscript{−} spin when the spin-polarising effect of the laser is off. This enables weaker power microwaves to de-polarise the spin, resulting in less power broadening of the ODMR spectra \cite{95} whilst still maintaining full optical contrast. It is possible to also perform microwave free ODMR, by using an applied magnetic field that Zeeman shifts the lower branch of the spin resonance towards zero-frequency, the so called ground state level anti-crossing \cite{96, 97, 98, 99, 100} at a magnetic field of $B = D/\mu_B g = 1025$ G.

The NV\textsuperscript{−} centre’s long spin coherence time enhances measurement sensitivity, since more phase can be accumulated in a single shot before the spin decoheres. Pulsed ODMR techniques take advantage of this to perform sensitive time dependent measurements. Since the NV\textsuperscript{−} centre is a spin triplet, a small bias magnetic field is usually applied to split the degenerate spin $m_s = \pm 1$ levels. Then transitions are driven between the $m_s = 0$ spin projection and either the $m_s = -1$ or $m_s = +1$ spin projections. As such, the system behaves as a two level scheme similar to those commonly represented on the Bloch sphere \cite{51}. The following descriptions assume that a single spin transition is selected, say between $m_s = 0$ and $m_s = +1$.

To determine the Rabi frequency ($\Omega$), the electron spin is initialised into the
2.1. INTRODUCING THE NITROGEN-VACANCY (NV) CENTRE

Figure 2.6: ODMR spectra showing the effects of power broadening on the three $^{14}$N hyperfine lines. This measurement was taken from an ensemble of NV$^-$ centres with a small copper wire ($\geq 50 \mu m$) delivering the microwave power. The dBm values represent the power of the microwaves prior to entering a 50 W amplifier. The separation of the two $m_s = \pm 1$ levels is due to a small applied magnetic field $B_{NV} \sim 15$ G.
$m_s = 0$ state via a spin polarising laser pulse. A resonant microwave pulse of varying length $\tau$ is then applied to drive the spin between the $m_s = 0$ and $m_s = +1$ spin states, on the Bloch sphere this rotates the state vector by an angle $\Omega \tau$ between the Bloch sphere poles. The final detection laser pulse reads out the spin state $m_s = 0$ projection via the spin state dependent optical contrast. The spin state is determined by the first $\sim 300$ ns of fluorescence normalised to the remaining part of the detection pulse ($\sim \mu$s) as shown in figure 2.7. Only the $\sim 300$ ns of the fluorescence is used as the system is spin-polarised by then and the initial spin population is lost. The normalisation is to account for any slow fluctuations in fluorescence, usually from a drift of optical focus.

For a Ramsey measurement, a $\pi/2$ pulse (of length $t = \Omega/(\pi/2)$) is applied to drive the spin from $m_s = 0$ to equal superposition of $m_s = 0$ and $m_s = +1$, this can be described in ket form as $|0\rangle \rightarrow \frac{1}{\sqrt{2}}(|0\rangle + i|1\rangle)$. The state is then allowed to evolve for a time $\tau$, picking up a phase due to some detuning $\delta$ giving the state $\frac{1}{\sqrt{2}}(|0\rangle + ie^{i\delta\tau}|1\rangle)$ before another $\pi/2$ pulse drives to $m_s = +1$. A laser then reads out the projection of $m_s = 0$ giving a population $P_{m_s=0} \propto \sin \Phi$ where $\Phi$ is the total accumulated phase $\Phi = \int_0^\tau \delta dt = \delta \tau$. This is an interferometry measurement where the accumulated phases of the $m_s = 0$ and $m_s = +1$ spin levels are interfered resulting in Ramsey fringes. This method gives the highest sensitivity for DC measurements of small detunings.

The spin-echo measurement is the same as the Ramsey except for the $\pi$ pulse half-way between the $\pi/2$ pulses. This $\pi$ pulse flips the spin state, 

$$\frac{1}{\sqrt{2}}(|0\rangle + ie^{i\delta\tau/2}|1\rangle) \rightarrow \frac{1}{\sqrt{2}}(i|1\rangle - ie^{i\delta\tau/2}|0\rangle).$$

The state then evolves again for a time $\tau/2$, 

$$\frac{1}{\sqrt{2}}(i|1\rangle - ie^{i\delta\tau/2}|0\rangle) \rightarrow \frac{1}{\sqrt{2}}(ie^{i\delta\tau/2}|1\rangle - ie^{i\delta\tau/2}|0\rangle).$$

The population is then read out using a $\pi/2$ pulse and laser detection pulse, resulting in an $m_s = 0$ spin projection of $P_{m_s=0} \propto \cos \Phi$, where $\Phi = \int_0^{\tau/2} \delta dt - \int_{\tau/2}^\tau \delta dt$. If the detuning $\delta$ is quasi-static over the time period $\tau$ then the net phase accumulation is cancelled out by the $\pi$ pulse. However, if the detuning varies with a period similar to pulse timing ($\tau$) then the net phase is not cancelled by the $\pi$ pulse. This is useful to measure AC signals and to remove the detrimental effect of slowly evolving noise, increasing the effective measurement time. The sequence is most sensitive to frequencies $f \sim \frac{2\pi}{\tau}$. Higher order spin-echo sequences such as CPMG [101], XY-8 [102],
UDD [103] can be used. These sequences all use a longer pulse train of periodic $\pi$ pulses with differing microwave phases at each pulse. The CPMG sequence replaces the single $\pi$ pulse in a spin-echo sequence with $N \pi$ pulses separated by the same $\tau$. The XY-8 sequence is the same as the CPMG except the phase of each $\pi$ pulse alternates by 90°, usually labelled by $X$ and $Y$. The UDD sequence is similar to XY-8 except the placement of the pulses is not at regular increments of $\tau$ but at some optimal timing, determined using models of the system and noise [104]. These methods increase measurement time even further by routinely decoupling the spin state from the environment, as a consequence they also reduce the sensing frequency bandwidth [53].

The effect of decoherence on these measurements results in signal modulated by an envelope decay function due to the dephasing of the electron spin. For a Ramsey measurement, this is characterised by a Gaussian decay envelope with the resulting signal is $S = C_1 + C_2 e^{-t/T_2^*} \sin \Phi$, with a characteristic time $T_2^*$. $C_1$ and $C_2$ are experimental parameters dependent on the photon count rate and the optical spin contrast. For a spin-echo measurement the signal is an exponential decaying envelope with a characteristic time $T_2$, giving $S = C_1 + C_2 e^{-t/T_2} \sin \Phi$. Note that the exact expression of the dephasing envelope depends on the nature of the dephasing interaction [53, 54] and other non-exponential decays in signal may be more appropriate.

The nuclear spins surrounding the NV centre, have a small magnetic nuclear spin that creates a magnetic field that the NV$^-$ is sensitive to too. Conversely, the magnetic field created by the electron spin can be used to control the nuclear spin [17]. This hyperfine interaction allows for the spin state of surrounding nuclei to be initialised, read out and controlled using the NV$^-$ electron spin. This allows for the NV$^-$ spin population to be stored on the nuclear spin. Storing and swapping the electron spin-state with the much longer lifetime of the nuclear spin is useful to gain more measurement time for sensitive magnetometry [9, 106, 107], quantum registers [20, 21, 19] or for quantum memories [26, 24, 25].
Figure 2.7: Example pulse sequences; upper is Rabi measurement; centre is Ramsey measurement; and lower is spin-echo measurement. Ramsey and Spin-echo data taken with permission from Childress et al [105]. Ramsey signal shows a beating with the three $^{14}\text{N}$ hyperfine frequencies. Spin-echo signal shows the collapse and revivals due to the $^{13}\text{C}$ spins effecting the electron spin.
2.1.3 Sensitivity

In general, the sensitivity of a measurement is dependent on the minimum signal \( S \) that can be detected and the effect a desired measurable quantity \( J \) has on that signal. As shown in figure 2.8, if the minimum detectable change in the signal \( S \) is given by the uncertainty in that signal \( \sigma_S \), then the minimum detectable change in the quantity \( J \) is,

\[
\delta J = \sigma_S \left( \frac{dS}{dJ} \right)_{\text{max}}^{-1}.
\]  

(2.3)

For pulsed measurements the signal can be optimised so that the maximum gradient \( dJ/dS \) is always achieved [54]. In general, the experimental uncertainty in signal from an NV$^-$/centre is photon shot-noise limited only. As such, the uncertainty of the signal improves with the number \( N \) of repeated measurements or photons collected \( \sigma_{\text{int}}/\sqrt{N} \), where \( \sigma_{\text{int}} \) is the intrinsic uncertainty of a single measurement. This uncertainty \( \sigma_{\text{int}} \) is due to factors such as the observable optical spin contrast, the collection efficiency and the rate of emission. For pulsed measurements of duration \( \tau \), the number of repeated measurements is \( N = T_{\text{tot}}/\tau \). The sensitivity is defined as \( \eta_J = \delta J \sqrt{T_{\text{tot}}} \) giving,

\[
\eta_J = \frac{\sigma_{\text{int}}}{\sqrt{T_{\text{tot}}/\tau}} \left( \frac{dS}{dJ} \right)_{\text{max}}^{-1} \sqrt{T_{\text{tot}}}
\]

\[
= \sigma_{\text{int}} \sqrt{\tau} \left( \frac{dS}{dJ} \right)_{\text{max}}^{-1}.
\]  

(2.4)

For example, when applying DC magnetometry using a Ramsey measurement sequence, the spin accumulates a phase \( \Phi = \delta \tau \), where \( \delta \) is the detuning caused by the

\[ S \]

\[ \sigma_S \]

\[ \delta J \]

\[ J \]

Figure 2.8: Depiction of sensitivity of a measured quantity \( J \) due to the signal \( S \) and signal uncertainty \( \delta_S \).
magnetic field $B$, giving $\delta = g\mu_B B/\hbar$. The fluorescence signal is sinusoidally dependent on the accumulated phase $S \propto \sin \Phi$ \cite{54}. For small detunings, the sinusoidal dependence of the accumulated phase $\Phi$ on the signal $S$ may be approximated as linear, so $S \approx \Phi \approx g\mu_B \tau B/\hbar$. This gives the field sensitivity,

$$\eta_B = \frac{\hbar \sigma_{\text{int}}}{g\mu_B \sqrt{\tau}}. \quad (2.5)$$

A Ramsey measurement is optimised for a measurement time $\tau = T_2^* \cite{53, 54}$ and the experimental factors contained in $\sigma_{\text{int}}$ are often re-expressed as $\sigma_{\text{int}} = 1/K$, a 30% spin contrast and a high-NA objective giving a photon count rate of approximately 300 kHz, give $K \approx 0.01$. This gives the final sensitivity expression,

$$\eta_B = \frac{\hbar}{K g\mu_B \sqrt{T_2^*}}. \quad (2.6)$$

In general, the AC and DC sensitivity due to change in the spin resonant frequency $D$ due to some quantity $J$ is \cite{31},

$$\eta_{J_{DC(AC)}} = \left(\frac{2\pi K dD}{dJ} \sqrt{T_{DC(AC)}}\right) \quad (2.7)$$

where a Ramsey sequence is used for DC with $T_{DC} = T_2^*$ and spin-echo sequence is used for AC with $T_{AC} = T_2$. The sensitivities to commonly measured quantities are shown in table 2.3.

When measuring an AC signal, the frequency resolution is determined by how long the measurement can be coherently performed. As such, the frequency resolution using a spin-echo or similar measurement is limited to $1/T_2$; although longer train pulse sequences such as CPMG or XY-8 give sharper frequency resolution \cite{108, 109}. Other methods utilise tricks to enhance the measurement time such as using the population lifetime ($T_1$) and correlation spectroscopy \cite{110, 111}, using nearby nuclear spins as a quantum memory \cite{112, 113, 114} or by correlating the measurement with a classical clock \cite{115, 116}. These methods can, not only achieve much better frequency resolution, but can also significantly enhance the sensitivity as more time is spent measuring.
2.2 REVIEW OF MECHANICAL STUDIES

<table>
<thead>
<tr>
<th>Quantity</th>
<th>DC (AC) sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic Field [117]</td>
<td>110 (11) nT/√Hz</td>
</tr>
<tr>
<td>Electric Field [118]</td>
<td>20 (20) mV/µm/√Hz</td>
</tr>
<tr>
<td>Temperature [30]</td>
<td>40 (4) mK/√Hz</td>
</tr>
</tbody>
</table>

Table 2.3: Table of NV\(^-\) ground spin sensitivities to various measured quantities, the AC sensitivities was approximated as \(\eta_{AC} = \eta_{DC} \sqrt{T_2^*/T_2}\), for \(T_2^* \approx 100 \times T_2\), appropriate numbers are \(T_2^* \approx 10 \mu s\) and \(T_2 \approx 1\) ms.

2.1.4 ODMR and crystal orientations

The NV centre is aligned along a \(\langle 111 \rangle\) crystallographic direction, as such it has a well defined orientation with respect to the crystal. This gives eight uniquely orientated NV centres or four if ignoring inversion symmetry (swapping placement of N and V along the same axis), which is usually valid for many of the interactions considered in this thesis. These four directions would be \([111]\), \([\overline{1}1\overline{1}]\), \([\overline{1}1\overline{1}]\) and \([\overline{1}\overline{1}1]\); inversion is achieved by multiplying by a global factor of \(\times -1\) giving another four \([\overline{1}1\overline{1}]\), \([\overline{1}1\overline{1}]\), \([\overline{1}\overline{1}1]\) and \([11\overline{1}]\) making a total eight unique NV directions. This geometry affects measurements in multiple ways; (1) The laser polarisation \((\vec{E}_0)\) affects the optical excitation of the NV centres electronic dipole \((\vec{d})\) via the standard dipole perturbation \(V = -\vec{d} \cdot \vec{E}_0\); (2) Similar to the electric dipole and optical excitation the magnetic dipole \((\vec{\mu})\) of the spin is excited when microwaves \((\vec{B}_0)\) are applied during ODMR measurements with a similar perturbation; (3) For almost all measurements there is usually an applied DC field (usually magnetic but possibly an electric field or strain) that shifts the energy levels. This perturbation is usually orientation dependent, for example the Zeeman shift of the ground-state spin levels is from the perturbation \(V = \vec{S} \cdot \vec{B}\). For weak fields this gives the angular dependence of the spin-resonances of \(\pm g\mu_B S_z \cos \theta\). For a single NV this angular dependence is useful to determine which one for orientations a particular NV has, for ensembles all orientations are examined at once, as such, this angular dependence is used to separate the signal from each orientation in a single spectra. In a similar fashion the previously mentioned optical excitation can also be used to distinguish certain NV orientations via the polarisation of the excitation laser.

2.2 Review of mechanical studies

Studying the interaction of solid state defects with crystal stress provides an approach to probe the nature of the defect’s structure. Davies and Hamer [45] per-
formed the seminal uniaxial stress study of the optical zero-phonon line of the then unknown NV centre. From observing the splitting behaviour of the degenerate $^3E$ excited state triplet, the NV$^-$ optical transition was identified as $A \leftrightarrow E$, thereby establishing its symmetry as trigonal ($C_{3v}$) and supporting prior speculation that it was an substitutional nitrogen with an adjacent vacancy. In addition to the work by Davies and Hamer on the visible ZPL, the mechanical interaction of the infrared zero-phonon line [56] and visible NV$^0$ zero-phonon line [65] have been studied using uniaxial stress. In each study new and fundamental information about the symmetry and electronic configuration of the NV centre were determined.

Since the emergence of spin-based quantum applications of the NV$^-$ centre, there has been renewed interest in the effect of crystal stress on the NV centre, in particular the spin-mechanical interaction. The NV$^-$ centre’s excellent electron spin coherence properties [84] and the ability to construct ultra-high quality factor (Q) single crystal mechanical resonators [42, 41] present exciting possibilities for NV-mechanical coupled systems. For example, an NV-mechanical oscillator coupled system may possibly be used to perform phonon cooling or phonon lasing [119]. This could allow for investigations into non-classical vibrations and zero-point motion of macroscopic objects - a fundamental test of the limits of quantum mechanics. Spin-squeezing could be mediated by spin-mechanical interactions [120, 121] allowing for a highly correlated spin state and enhanced spin-based metrology with sensitivity beyond the shot noise limit [122]. Spin-mechanical interactions could be used as an alternative means to measure forces at the nanoscale, possibly allowing for sensing of magnetic fields, electric fields, temperature and force sensing with the same device.

Hybrid NV spin-mechanical systems have also been realised, in which the NV is coupled via a magnetic field to a mechanical oscillator [123, 124, 125, 126, 127]. In these cases, a large magnetic field gradient is required. This spatially couples the mechanical oscillator’s motion to the NV spin resonance via Zeeman interactions. These measurements have shown unique tests of spin-coupled systems and sensitive spin-based detection of mechanical motion. However, the thermomagnetic stability of such large field gradients at the nanoscale and room temperature is problematic and can result in a loss of spin coherence or sensitivity [123]. This limits their force sensing abilities. These examples do not provide new information about the spin-mechanical interaction in diamond itself or any spin-phonon interactions. Furthermore, when using a large magnetic field gradient it is not possible to alternate between magnetometry, thermometry or electrometry without removing the magnetic field, limiting the ease in which the device can alternate sensing roles. There is strong interest in these types of coupled quantum-mechanical measurements.
which explore non-classical motion. However, the limitations of hybrid magnetic-NV spin-mechanical devices motivates that the inherent NV spin-mechanical interaction should be studied as a possible alternative to explore non-classical motion with the NV centre.

Doherty et al [32] described the effects on the ground state triplet due to applied hydrostatic pressure with an explanation that discussed the displacement of the nuclei around the defect and their effect on the electrons’ behaviour. The change in nuclear position effects the electrostatic potential seen by the electrons and changes the electron orbitals - affecting the spin density and spin-spin interaction. For uniaxial stress (non-hydrostatic), the physical picture remains the same. However, the symmetry of the defect requires that stresses in different crystal directions will have different couplings to the ground state spin. To date no formal and complete characterisation of the spin-mechanical interaction of the $^3A_2$ ground state triplet of the NV$^-$ centre has been performed. There have been multiple descriptions of the spin-mechanical interaction of the ground state spin in several papers [32, 33, 34, 35, 36, 37, 38], however, part I of this thesis will show that these descriptions have either been incomplete or interpreted incorrectly.

The first study of the dependence of crystal stress on the ground state spin resonance ($D$) was by MacQuarrie et al [36] using an ensemble of NV centres in a diamond integrated microelectromechanical (MEMS) device capable of generating high frequency ($>1$ GHz) stress powerful enough to drive transitions between NV$^-$ spin levels. This is the first demonstration of using stress to control the spin-state on an NV centre. Their model used a simple two parameter coupling, requiring transverse and axial susceptibility parameters. As will be described later, this can phenomenologically explain the behaviour of the spin-state but the parameters determined are not unique and don’t completely represent the entire inherit spin-mechanical interaction. The assumption of a single transverse spin parameter requires that the $x$ and $y$ components of the interaction are equal, an assumption that isn’t generally true. MacQuarrie et al’s determination of the magnitude of the stress relied on assuming that the device acted like a single harmonic oscillator whose mechanical properties were estimated from the mechanical quality factor ($Q$). The $Q$ factor was estimated from the microwave power reflected from the driving piezo element. This relies on the assumptions that there are no other losses or non-linearities not represented by the reflected microwave power. As such, the measured stress could be systematically incorrect and any discrepancy would be hard to test. The stress in the driving direction was used to estimate the transverse stress as there was no way to measure transverse vibrations in such a one dimensional structure. Any concept
of shear stress was also ignored.

Doherty et al [32] performed hydrostatic ground state ODMR measurements of the spin-mechanical interaction of single and ensembles of NV− centres within a diamond anvil cell (DAC). They saw a linear shift of the spin resonance and optical zero-phonon line under pressures up to 60 GPa. The linear shift was described using a semi-classical approach that considered the spin-density and orbital-probability density changes due to the isotropic movement of the carbon nuclei under hydrostatic pressure. The shift rate was found to be 14.58(6) MHz/GPa and a room temperature DC pressure sensitivity $\eta \sim 0.6$MPa/$\sqrt{\text{Hz}}$. This measurement can only reveal one part of the spin-mechanical interaction as it is not possible to extract the information from different stress directions.

Teissier et al [33] performed AC and DC measurements of the spin-mechanical interaction of single NV centres within a diamond cantilever. They also used a two parameter model that was based on transverse and axial susceptibility values which ignored shear and treated $x$ and $y$ equally. They estimated the strain at the NV position within the cantilever using Euler-Bernoulli beam theory to determine the susceptibility parameters. However, the rotation formalisms they used to describe the stress in the NV coordinate system were based on vector and not tensor rotations. As such, this generated an incorrect expression for the stress in the direction of the NV axis.

Ovartchayapong et al [34] performed AC only strain measurements of single NV centres within a diamond cantilever. They too used a two parameter model that ignored shear strain and treated the $x$ and $y$ susceptibilities equally. They also determined the strain at the NV centre location in the cantilever using elastic Euler-Bernoulli beam theory. They found similar behaviour to Teissier et al, however, their susceptibility parameters did not agree, possibly due to the incorrect rotations used by Teissier et al. These parameters are the most often cited as the correct spin-mechanical interaction parameters by other publications.

Barfuss et al [35] performed AC strain measurements of single NV centres within a diamond cantilever. They used the same two parameter model presented by Teissier et al [33] and focussed on demonstrating mechanical driving between spin levels and presented a dressed state Hamiltonian of the coupled strain-spin system. Using a Ramsey style experiment, they showed an enhancement of the spin-coherence time due to this coupling protecting the spin level. This is because the strain-coupled eigenstates are an equal superposition of the $m_s = +1$ and $m_s = -1$ spin levels, as such these eigenstates are, to first order, insensitive to magnetic field noise. This is similar to other systems where perturbations are operated at a
2.2. REVIEW OF MECHANICAL STUDIES

turning point and interactions are reduced to a quadratic dependence [128].

MacQuarrie et al published another work based on their ensemble MEMS device [37]. They used the spin-mechanical susceptibility parameters published by Ovartchaiyapong et al [34] and focussed on investigations of coherently driving the spin levels mechanically. Like Barfuss et al [35] they demonstrated that when mechanically driving their spin system coherently an increase of the spin coherence time is observed.

Meesela et al [38] demonstrated the fabrication of a high $Q$ single crystal cantilever oscillator. Studying an ensemble of NV centres within their device they demonstrated AC and DC spin-mechanical coupling. They used the same two parameter model that has been shown in the previous papers.

Examples of ultra-high $Q$ factor cantilevers have been demonstrated by Tao et al [41] and Ovartchaiyapong et al [42] that show single crystal diamond is an excellent material for very high quality mechanical resonators. Tao et al demonstrated a $Q > 10^6$ at room temperature, which surpasses the achievable state of the art for conventional silicon cantilevers. This is significant because a high $Q$ device allows for a stronger interaction and sensitive spin-mechanical metrology with better spectral and amplitude sensitivity. A higher $Q$ also allows for stronger coupled spin-phonon devices for spin-squeezing or zero-point motion experiments.

Unfortunately, the previous publications detailing the spin-mechanical interaction all use a similar model that oversimplifies the spin-mechanical interaction, leading to inconsistencies in the documented susceptibility parameters [33, 34]. This is in part due to the description of the ground state Hamiltonian by Doherty et al [129] which compared the effect of strain to an electric field as they are both coefficients of the same spin-operators in the Hamiltonian. However, the spin-mechanical coupling coefficients represented in the Hamiltonian are not single constants as often assumed, but are multi-dimensional parameters that depend significantly on the applied stress tensor and the orientation of the NV centre being investigated. This fundamental difference is due to the degrees of freedom of a mechanical strain versus an electric field. An electric field at an NV centre can be represented as a three component vector $(E_x, E_y, E_z)$ and its effect upon the NV centre can be described by arguments of symmetry with just an axial and a transverse component. The stress or strain at an NV centre however is represented by a $3 \times 3$ symmetrical tensor with 6 unique elements ($\sigma_{xx}, \sigma_{yy}, \sigma_{zz}, \sigma_{yz}, \sigma_{xz}, \sigma_{xy}$) whose effect cannot be broken down symmetrically into just axial and transverse components. Hughes and Runciman [130] presented a clear way to represent the stress tensor using components that transform as the irreducible components of the centre’s trigonal $C_{3v}$ symmetry. From this treatment,
symmetry requires that four parameters are needed to describe the spin-mechanical interaction of the trigonal defect within a cubic crystal. This was the model used by Davies and Hamer [45] when they first identified the NV centre as an $A \leftrightarrow E$ trigonal defect that was likely to be an nitrogen-vacancy pair. This thesis extends the model outlined by Hughes and Runciman [130] and Davies and Hamer [45] to include a description of the NV$^-$ spin-mechanical interaction.

In the defence of the previous publications, using only two parameters is justifiable as two parameters can phenomenologically describe the spin-mechanical behaviour seen in one measurement. Each of those experiments applied stress in only one crystallographic direction repeatedly and that only produces two pieces of information - a splitting and a shift of the spin resonance. These two pieces of information were designated to the transverse and axial coupling parameters respectively. However, to measure the entire intrinsic interaction, multiple crystal orientations have to be used and none of the previous studies reported to do that. If one of the previous studies performed measurements in differently orientated crystals then it would be apparent that simple rotations of the stress tensor for the differently orientated crystals would not provide self consistent results based on any two parameter model.

2.3 Review of temperature studies

There are fundamental links between the effects of temperature and the effects of stress on a solid body. For example, the thermal expansion of a solid is opposite to hydrostatic compression. As such, many of the mechanical physical processes mentioned in part I are shared with the behaviour of the NV$^-$ centre with respect to changes in temperature.

Like the mechanical interaction, the thermal interaction of the optical zero-phonon line has also been well studied and is accurately understood. Again Davies performed some of the very first studies of the thermal properties of the NV$^-$ optical ZPL transition [63]. Similar measurements were performed by Collins et al [68] around the same time and agreed with Davies. Davies used a model that included both the thermal expansion of the crystal and the temperature dependence of the electron-phonon interaction of those energy levels.

Acosta et al [29] investigated the temperature dependence of the ground state zero-field splitting $D$ ($\sim 2.87$ GHz) in NV ensembles between 280-330 K. They described the effect as linear changes in the zero-field splitting. Acosta et al found that the temperature dependence was sample independent, so it should be intrinsic to the NV defect itself and only changes in the shift of the resonance and no splitting
2.3. REVIEW OF TEMPERATURE STUDIES

is apparent. They reasoned that since the origin of the zero-field splitting \( D \) is due to dipolar spin-spin interactions of the unpaired spin density of the defect, then any changes to \( D \) due to temperature should result from changes in that spin density. They found that the behaviour did not agree with the \( \sim 1/r^3 \) dependence expected for the thermal expansion of the crystal and the unpaired spin density. They were careful to include electronic orbitals that conformed to the \( C_{3v} \) symmetry of the defect in their expansion of the nuclear positions.

Chen et al. [131] performed very similar measurements but for low temperature \( T < 300 \) K and also included observations of the fluorescence spectra of NV\(^-\) and NV\(^0\). They noted the similarity of the fluorescence spectra and the spin resonance temperature dependence and that the behaviour did not agree with \( \sim 1/r^3 \) dependence expected from a change in the dipolar interaction due to thermal expansion. They documented a fifth order polynomial to describe the observed behaviour. The similar temperature dependence behaviour of the optical and spin resonances suggested that the interactions share certain properties and the previous studies of the visible ZPL [63, 68] should be drawn upon to aid in understanding the behaviour of the spin resonance and the infra-red ZPL.

Toyli et al. [31] measured the NV\(^-\) ODMR characteristics from room temperature to 700 K using single centres. The changes in fluorescence, ODMR optical spin-contrast, excited state lifetime and \( T_2^* \) as a function of temperature were recorded. These results can be combined to provide useful information of the expected temperature sensitivity over a wide range of temperatures, from 0.02 to 100 mK/\( \sqrt{\text{Hz}} \) between room temperature and 600 K. The shift of the spin resonance \( D \) was explained using a third order polynomial in temperature. The polynomial origin of the temperature dependent energy shift is not explained in detail. The polynomial values provided were measured for high temperatures and don’t show experimental agreement with low temperature values published by Chen et al [131].

Despite this lack of knowledge of the fundamental cause of this temperature dependence, the thermal shift of the spin resonance \( D \) has been usefully employed to perform demonstrations of accurate nano-thermometry. Neumann et al. [27] demonstrated temperature sensitivities of \( \eta \sim 5 \) mK/\( \sqrt{\text{Hz}} \) for single NV centres in bulk diamond and \( \eta \sim 130 \) mK/\( \sqrt{\text{Hz}} \) for ensembles of NV centres in nanodiamonds. They designed a unique and useful pulse sequence that drove the spin levels between both \( m_s = 0 \) and the \( m_s = +1 \) and \( m_s = -1 \) spin levels separately. This measurement was sensitive to changes in the shift of the \( D \) resonance, but not the splitting of the \( D \) resonance which could be caused by unwanted magnetic fields. This process was named the \( D \)-Ramsey sequence. This method also cancels the
contribution from magnetic field noise which has a dephasing effect on the NV spin, this allows for measurement times approaching $T_2$ as opposed to $T_2^*$ as is usual in Ramsey measurements, thereby increasing sensitivity by a few orders of magnitude.

Kucsko et al [28] performed measurements using ensembles of NV centres within nanodiamonds that were inside human embryonic fibroblast WS1 cells. They demonstrated sensitivities $\eta \sim 9 \text{ mK}/\sqrt{\text{Hz}}$ using a similar $D$-Ramsey sequence as Neumann et al. and observed the effects of heating on cell health simultaneously with NV based temperature measurements. Both studies used a linear $D$ shift parameter to monitor and calculate the temperature. This is probably valid over the small temperature ranges they investigated and justified as a more complete temperature dependence had not been published at the time. However, the temperature dependence is known to not to be linear over the full useful temperature range (mK - 600 K) of the NV centre and the full description should be used to take full advantage of the NV centre as a temperature sensor.

Toyli et al [30] also demonstrated high sensitivity thermometry and employed dynamic decoupling CPMG sequences using repeated $\pi$-pulses between the $m_s = 0$ and the $m_s = \pm 1$ levels separately to measure only the average shift $D$ of the two levels. This higher order sequence extends the interrogation time and limits the dephasing effects of $^{13}$C spin bath, reducing the requirement for isotopically pure samples. A temperature sensitivity of $\sim 10 \text{ mK}/\sqrt{\text{Hz}}$ was achieved.

To address the lack of fundamental understanding of the temperature shift, this thesis details a model that draws on the success of Davies’ vibronic model in explaining the visible ZPL and applies it to the infra-red ZPL, and the spin resonance $D$. This model and fitted parameters will be invaluable in modelling and understanding the temperature dependence of NV either for enhanced thermometry or to design experiments that remove the unwanted thermals shifts, important for high sensitivity magnetometry, electrometry or other metrology.

The hyperfine interaction of the $^{13}$C spins surrounding the NV centre have been well investigated and documented [17, 46, 74, 92, 132]. This interest is due to the very long coherence time of the nuclear spins [26] in diamond and the strong interaction with the NV$^-$ centre allowing for use of the $^{13}$C nuclear spins as qubits and the NV$^-$ spin as a quantum bus [133, 134]. The stronger interaction of the NV$^-$ with the $^{13}$C ($\sim 130 \text{ MHz} [46]$) compared to $^{14}$N or $^{15}$N ($< 5 \text{ MHz} [74, 91]$) is due to the unpaired spin density being localised at the carbon atoms [46, 74, 91] and an enhanced Fermi contact interaction. It is expected that this increased hyperfine interaction will result in stronger thermal hyperfine spin resonance shifts for NV centres with a first shell $^{13}$C. Also, since the first, second, third, etc, shell $^{13}$C can be uniquely
identified [17, 74, 92] this interaction can be used to probe the extent of the change of the spin density at different locations caused by thermal expansion and changes in the spin density distribution. Additionally, since the spin lifetime of the $^{13}$C is very long [26] increased temperature sensitivity using the hyperfine interaction may also be possible. This thesis investigates the possibilities surrounding the thermal changes of the $^{13}$C hyperfine interaction, in particular the use of this interaction as a nanoscopic probe of the extent of the NV$^-$ spin density.

Intense interest and research in the NV centre during the past two decades has left few remaining mysteries about the function of the NV centre. However, one significant deficiency is a complete understanding of the NV$^-$ singlet levels. In particular the lower ISC crossing from the lower singlet $^1E$ to the $^3A_2$. Similarly, another significant remaining mystery is the lack of measured fine structure of the neutral nitrogen-vacancy NV$^0$. It is believed that these unknown levels will have many properties in common, as they exhibit some similar behaviours.

The importance of rectifying these mysteries is clear. As already discussed the spin-polarisation and spin-readout mechanisms provided by the ISC are critical for the practical application of the NV$^-$ centre.

The upper ISC to the $^1A_1$ is a relatively well known two step process, firstly a spin-orbit mediated transition from the $^3E$ to an excited vibrational level of the $^1A_1$ state occurs. Secondly, phonon-phonon interactions lead to a decay to the ground $^1A_1$ vibrational level. From here the system either radiatively decays by emitting an IR photon or non-radiatively decays through vibrations to the $^1E$. However, the lower ISC from $^1E$ to $^3A_2$ is not as well understood. This poor understanding is a direct consequence of limited experimental knowledge of the singlet levels. The net ISC rate has been measured [83], however, the relative amounts to the $m_s = 0$ and $m_s = \pm 1$ and the underlying mechanism are not known.

In fact, there are several other mysteries surrounding the singlet levels which indicate something unexplained about their nature. Firstly, the absorption and emission spectra of the singlet IR transition have drastically different phonon sidebands [56, 67]. The emission band does not resemble the NV$^0$ and NV$^-$ emission/absorption spectra, as would be expected for simple linear interactions with $A_1$ phonons. The absorption band of the NV$^-$ IR ZPL has been analysed by Kehayias et al [67] in comparison to the NV$^-$ visible absorption band and relatively strong agreement of the phonon structure was used to analyse the phonon density of states and existence of local modes of the $E \rightarrow A$ optical transition. This disagreement between the emission and absorption phonon sidebands highlights that there are unexplained vibrational processes occurring the $^1E$ which are not present in the other
levels of the NV centre.

Secondly, it is predicted that there should not be a transverse strain splitting of the IR ZPL from changes in the electron-nuclear Coulomb interaction as the nuclei surrounding the NV centre deform. This is because the two electrons occupying the $e$ orbitals should each effectively raise and lower in energy and the effect cancel out. However, the IR ZPL strain parameters have been determined experimentally by Rogers et al. [56, 66] and are similar in magnitude to the visible NV$^-$ and NV$^0$ ZPL strain parameters [45, 65]. To explain this discrepancy, Rogers et al argued that this was due to the Coulomb electron-electron repulsion effects between the electrons in the two $e$ orbitals. Rogers et al states that this electron-electron Coulomb term must be similar in magnitude to the one electron Coulomb interaction to agree with strain response seen in the NV$^0$ and NV$^-$ visible transitions. Although this description satisfactorily explains the larger than expected strain shift, its presence is still mysterious enough to deserve special mention.

Thirdly, there is an emergence of a new feature in the emission spectra under strain at 115 cm$^{-1}$ from the IR ZPL. The origin of this feature has been previously explained to be similar to other extra features in trigonal defects in diamond [65] and caused by a dynamic Jahn-Teller interaction. The linear Jahn-Teller interaction between the $E$ electronic states with $E$ vibrations, results in the vibronic coupling that forms the vibronic states $E \otimes E = A_1 \oplus A_2 \oplus E$. The degeneracy of the $A_1$ and $A_2$ vibronic levels are lifted by quadratic Jahn-Teller interactions, under strain the lower $A_1$ level can be seen in the emission spectra of the NV$^-$ IR ZPL. A similar extra feature is seen in the $2E$ ground state of NV$^0$ under uniaxial stress at 110 cm$^{-1}$ [65]. These features are strong evidence that dynamic Jahn-Teller processes are present in the singlet $^1E$. Curiously, this 115 cm$^{-1}$ feature has an energy (14 meV) which matches the one-phonon characteristic energy in the decay model used by Acosta et al (15 meV [64]) and Robledo et al (16.6 meV [83]) to explain the metastable singlet state lifetime. Therefore, this feature could play a significant role in the lower ISC.

Finally, the temperature shift of the IR ZPL is observed to be quite small [135]. The temperature shift is a combination of a thermal expansion shift and quadratic electron-phonon interactions with $A_1$ modes. Since the strain shift of the IR ZPL is significant [66], this requires that quadratic electron-phonon interaction with $A_1$ modes be small such that the total temperature shift is small. Such that their contribution to the ZPL shift is small. This is unlike what is seen in the NV$^-$ visible ZPL temperature shift. Given the presence of the above Jahn-Teller uniaxial feature, it is possible the $^1E$ couples more strongly to $E$ vibrations than to $A_1$.
vibrations. The small Jahn-Teller in the NV$^-$ $^3E$ [136] and a larger thermal shift implies that the opposite is true for the NV$^-$ $^3E$. That is, it couples more strongly to $A_1$ vibrations than to $E$ vibrations.

Given the significance of the role the ISC plays in the practical application of the NV$^-$ centre, efforts to resolve the lack of understanding in this area will be beneficial. Either for more accurate modelling of the system or for engineering of the defect to have more desirable spin-polarisation and spin read-out properties. For example, a more significant optical spin contrast.

Similar to the singlet states, the NV$^0$ charge state of NV centre is much less well understood than the NV$^-$ charge state. Mysteriously, the NV$^0$ centre has no observable magnetic fine-structure in the ground $^2E$ state doublet ($S = \frac{1}{2}$), measured via electron paramagnetic resonance or resonant photoluminescent excitation (PLE). However, a $S = \frac{3}{2}$ EPR signal has been seen in the metastable $^4A_2$ quartet level of NV$^0$ which showed spin-polarisation under optical pumping at energies above a 2.2 eV threshold [137].

The charge state of NV is unstable and often fluctuates between the NV$^0$ and NV$^-$ [60, 61]. This can be detrimental for measurements using NV$^-$ and much effort is made to reduce this instability [138, 139, 140]. Manipulation of this charge state has been demonstrated [141], and its use for electrical spin-readout [142] and data storage [143, 144] demonstrated. Ionisation of NV$^-$ to NV$^0$ and NV$^+$ has been investigated because the removal of the electron spin from the NV centre can improve the nuclear spin lifetime [39]. Despite this interest in NV$^0$ the spin structure of the NV$^0$ ground state has not been observed. However, Waldherr et al [61] have measured an nitrogen NMR signal due to the NV$^0$ using photoionisation and the NV$^-$ spin to read-out this signal. Only the NMR signal from one spin $-1/2$ level was observed, suggesting some sort of spin polarisation was occurring. Although this is a measurement of some NV$^0$ magnetic fine structure, it is not a direct measurement and doesn't explain why fine structure isn't seen in EPR or PLE.

Explanations for why there is no apparent NV$^0$ ESR could be (1) the orbital angular momentum has been quenched by a Jahn-Teller interaction. In the case of strong Jahn-Teller with a single $E$ local mode the mixing of the electronic properties of the $E$ state amongst the new vibronic states results in a reduction of the observable angular momentum. This effect is called a Ham reduction [145]. If instead there is a weak Jahn-Teller coupling with a bath of $E$ acoustic modes and that coupling is faster than spin-orbit, this results in fast averaging over orbital states reducing the apparent orbital angular momentum. This effect is often called motional narrowing and is used to explain the difference in observable fine-structure
between high and low temperature in the NV$^{-}$ $3E$ level [97]. As seen with the $3E$ this effect should be temperature dependent, with less orbital averaging occurring at low temperature. For both of the previous two cases, the strong quenching of the angular momentum results in a level that is essentially the same as $g = 2$ and $S = 1/2$ spin which would be difficult to differentiate from the large P1 signal in diamond EPR spectra. (2) There is a weak Jahn-Teller interaction with a bath of acoustic $E$ modes that is slower than the spin-orbit interaction. In this non-motional narrowing spin-resonance broadens with a linewidth equal to the phonon scattering rate. This could broaden the lines beyond detection. Or simply, (3) the EPR simply hasn’t been observed as efforts to find it have not looked in the right parameter space or its signal was not noticed.

Similar to the IR ZPL, a dynamic Jahn-Teller distortion is demonstrated in the uniaxial measurements of Davies [65] of the NV$^0$ ZPL which show an extra emission feature under strain. This feature is at a similar energy of $\sim 110$ cm$^{-1}$ above the lowest $2E$ state. Due to the similarities between the NV$^{-}$ IR $1E \leftrightarrow 1A_1$ transition and the NV$^0$ $2E \leftrightarrow 2A_2$ it is hoped that measurements which can determine more information about NV$^0$ will also shed light on the behaviour of the singlet states and vice-versa.

Magnetic circular dichroism (MCD) is an optical spectroscopy technique that is very sensitive to the magnetic properties of an optical transition in the presence of a magnetic field. MCD measurements, in conjunction with excitation spectroscopy were used by Reddy et al [47] to determine the order of the NV$^-$ triplet states (determining that $3A_2$ is the lower state) and proving that the triplet states were not the metastable states as postulated by Loubser and Van Wyk [46]. In this measurement Reddy et al also determined the $3E$ orbital $g$-factor to be 0.1 and spin-orbit parameter $\lambda$ to be 30 GHz, although the later was incorrectly measured by a factor of 6 and has been measured more recently to be $\lambda = 5.3$ GHz [146, 147]. The only other measurement of the $3E$ orbital $g$-factor was by Hanza$^{wa}$ et al [148], who measured the Zeeman shift of the ZPL in absorption at very high magnetic fields (150 T) and obtained a $g$-factor of 0.2.

MCD measurements of the NV$^-$ IR ZPL and the NV$^0$ ZPL will provide magnetic fine-structure information about the $1E$ and $2E$ states in the NV$^-$ and NV$^0$ charge states. This orbital information can supply the spin-orbit, spin and orbital $g$-factors, all of which provide fundamental behaviour about the level. Reduced orbital $g$-factors provide information about the quenching of orbital angular momentum, which in turn is often related to Jahn-Teller interactions [145, 149]. Similarly, spin-orbit is a fundamental parameter required to describe even the most basic.
function of the level.
Part I

Mechanical Interaction
CHAPTER 3

Description of the NV$^-$ spin-mechanical interaction

3.1 Contributions

The theoretical details of the spin mechanical interaction were developed by M.S.J. Barson, M.W. Doherty and N.B Manson.

3.2 Introduction

This chapter studies how the stress or strain in a crystal interacts with a defect within that crystal from a theoretical point of view. By using arguments of the symmetry of the crystal and the defect and comparing to similar systems the full spin-mechanical interaction within the NV$^-$ ground state Hamiltonian is described. Included are descriptions of how to change between describing the interaction with stress or with strain and how to rotate the coordinate system the of the stress or strain. This is included as some readers may be interested in applying these relationships to different crystal orientations or units.

3.3 Theoretical description

As discussed in chapter 2.2, the NV$^-$ spin-mechanical interaction description used in this work is similar to many different studies of defects in solid-state systems [45, 56, 66, 130, 150, 151, 152, 153, 154]. It appears that Kaplyanskii initially developed this method, which considers the symmetry of the crystal together with the symmetry of the defect and uses group theory to define the interaction. Kaplyanskii’s papers are mostly published in former USSR journals and are very hard to find [155, 156, 157, 158]. As such, this derivation is adapted from the works by Hughes and Runciman [130] and Davies and Hamer [45].
CHAPTER 3. DESCRIPTION OF THE NV- SPIN-MECHANICAL INTERACTION

In the group-theoretical approach of Hughes and Runciman [130], the first-order perturbation to the electronic states of a trigonal defect within a cubic crystal due to stress or strain can be written as

\[ V = \sum_{i,j} A_{ij} \sigma_{ij} = \sum_{kl} B_{kl} \epsilon_{kl}, \]  

(3.1)

where, \( \sigma_{ij} \) and \( \epsilon_{kl} \) are the stress and strain tensors, respectively, and \( A_{ij} \) and \( B_{kl} \) are electronic operators. \( A_{ij} \) and \( B_{kl} \) are linked by the components of the stiffness tensor \( C_{ijkl} \), \( B_{kl} = \sum_{i,j} A_{ij} C_{ijkl} \). The choices of working with stress or strain are essentially equivalent. For this work, stress was the most natural choice as we were applying a known force, not a known deformation as employed in other experiments. Details on converting between stress/strain units and coordinate systems are explained in section 3.4.

Considering a defect with trigonal symmetry, the interaction may be redefined in terms of irreducible representations \( V = \sum_{\Gamma,r} A_{\Gamma r} \sigma_{\Gamma r} \), where \( \sigma_{\Gamma r} \) is part of the stress tensor that transforms as the \( r \)th basis vector of the irreducible representation \( \Gamma \), such that [130]

\[ V = A_1 V_{A_1} + E_x V_{E_x} + E_y V_{E_y} + A_1' V_{A_1'} + E_x' V_{E_x} + E_y' V_{E_y}. \]  

(3.2)

There are two components of the stress tensor which transform as \( \Lambda_1 \), hence the two components \( A_1 \) and \( A_1' \), similarly for \( E_x \) and \( E_y \). The local distortions of these different components are shown in figure 3.1(b). These are the same as the normal modes of vibration for a \( C_{3v} \) molecule [159].

In the basis of states \( \{|A_1\rangle, |E_x\rangle, |E_y\rangle\} \) the electronic operators are

\[ V_{A_1} = |E_x\rangle \langle E_x| + |E_y\rangle \langle E_y| - |A_1\rangle \langle A_1| \]
\[ V_{E_x} = |E_x\rangle \langle E_x| - |E_y\rangle \langle E_y| \]
\[ V_{E_y} = -|E_x\rangle \langle E_y| - |E_y\rangle \langle E_x|, \]  

(3.3)
Figure 3.1: (a) Unit cell with coordinates labelled, \(XYZ\) and \(xyz\) are crystal and NV coordinates, respectively. The green N signifies the nitrogen and the pink V signifies the vacancy. (b) Symmetrised distortions of a trigonal defect (N - green, C - grey). The \(A_1\) component is like hydrostatic compression, the \(A'_1\) component is “pancaking” the defect but preserving rotational symmetry. The \(E_x\) and \(E_y\) components are breaking the rotational symmetry in the plane of the carbons, and the \(E'_x\) and \(E'_y\) are breaking the rotation symmetry out of the plane of the carbons \([160]\)

\[
A_1 = a_1 (\sigma_{XX} + \sigma_{YY} + \sigma_{ZZ}) \\
A'_1 = 2a_2 (\sigma_{YZ} + \sigma_{ZX} + \sigma_{XY}) \\
E_x = b(2\sigma_{ZZ} - \sigma_{XX} - \sigma_{YY}) \\
E'_x = c(2\sigma_{XY} - \sigma_{YZ} - \sigma_{XZ}) \\
E_y = \sqrt{3}b (\sigma_{XX} - \sigma_{YY}) \\
E'_y = \sqrt{3}c (\sigma_{YZ} - \sigma_{ZZ}),
\]

where \((x, y, z)\) refers to the defect coordinate system and \((X, Y, Z)\) refers to the crystal coordinate system, as shown in figure 3.1(a). For a trigonal defect like the NV centre, the \(z\) axis is defined by the centre’s axis of rotational symmetry and its \(x\) axis is defined by one of its reflection planes. The crystal coordinate system is defined such that \((X, Y, Z)\) are in the ([100], [010], [001]) crystallographic directions.

The stress susceptibility parameters of the NV centre’s optical transitions are well-established from previous optical spectroscopy under uniaxial stress \([45, 66]\). The optical transitions occur between the centre’s \(A\) and \(E\) orbital electronic states. Since the \(|0\rangle\) and \(|\pm 1\rangle\) spin states of the centre’s ground \(^3A_2\) level also transform as the \(A\) and \(E\) irreducible representations \([57]\), respectively, the above theory applies
without loss of generality. For these spin states, it is more natural to express the operators (3) in terms of dimensionless $S=1$ spin operators

$$V_{A1} = S_z^2 - \frac{2}{3}$$
$$V_{E_x} = - (S_x^2 - S_y^2)$$
$$V_{E_y} = S_x S_y + S_y S_x.$$  \hfill (3.5)

This allows the spin-mechanical interaction to be simply added to the ground state spin-Hamiltonian [57] to give

$$H = (D + M_z) \left( S_z^2 - \frac{2}{3} \right) + \gamma_e \vec{S} \cdot \vec{B} - M_x (S_x^2 - S_y^2) + M_y (S_x S_y + S_y S_x),$$  \hfill (3.6)

where $\gamma_e$ is the electron gyromagnetic ratio, $\vec{B}$ is the applied magnetic field and

$$M_z = a_1 (\sigma_{XX} + \sigma_{YY} + \sigma_{ZZ}) + 2a_2 (\sigma_{YZ} + \sigma_{ZX} + \sigma_{XY})$$
$$M_x = b (2\sigma_{ZZ} - \sigma_{XX} - \sigma_{YY}) + c (2\sigma_{XY} - \sigma_{YZ} - \sigma_{ZX})$$
$$M_y = \sqrt{3} b (\sigma_{XX} - \sigma_{YY}) + \sqrt{3} c (\sigma_{YZ} - \sigma_{ZX})$$  \hfill (3.7)

are the spin-mechanical susceptibility parameters.

Physically this behaviour can be explained by a stress-induced change to the spin-spin interaction, which arises from the distortion of the unpaired spin density. The spin-density is pictured in figure 3.2(a). It is tightly bound within the range of the closest carbons highlighting that only the local distortions mentioned so far need to be considered. This spin-spin origin of the spin-mechanical interaction is emphasised by the fact that the interaction can be neatly written as a change $\Delta \vec{D}$ to the zero-field spin-spin tensor $\vec{D}$

$$H = \vec{S} \cdot (\vec{D} + \Delta \vec{D}) \cdot \vec{S} + \gamma_e \vec{S} \cdot \vec{B},$$  \hfill (3.8)

where

$$\Delta \vec{D} = \begin{pmatrix}
-M_x - \frac{1}{3} M_z & M_y & 0 \\
M_y & M_x - \frac{1}{3} M_z & 0 \\
0 & 0 & \frac{2}{3} M_z
\end{pmatrix}.$$  \hfill (3.9)

Applying first-order perturbation theory to the above [129], the ground state spin resonance frequencies are

$$f_{\pm} = D + \delta \pm \Delta,$$  \hfill (3.10)
Figure 3.2: NV$^-$ spin density isosurfaces for $^3A_2$ and $^3E$. Taken with permission from Gali et al [92]. The grey atoms are carbons and the blue atom is the nitrogen. The clear clumping of spin-density is surrounding the vacancy. This strong localisation of the spin density is due to the confining electrostatic potential of the surrounding nuclei. As such, when the nuclei shift the spin-spin interaction of the spin-density will be affected.

where

$$\delta = M_z$$

$$\Delta = \sqrt{(\gamma_e B_z)^2 + M_x^2 + M_y^2}$$

It can be seen that an $A_1$ stress (only giving rise to $M_z$) results in only a shift of the spin resonances, whereas an $E$ stress that distorts the centre’s trigonal symmetry (giving rise to $M_x$ and $M_y$), splits the spin resonances. To describe the behaviour in any more detail, the applied stress needs to be further defined.

For a uniaxial pressure $P$ applied in the $\hat{P}$ direction, the stress tensor is $\sigma_{IJ} = P(\hat{P} \cdot \hat{I})(\hat{P} \cdot \hat{J})$, where $\hat{I}$ and $\hat{J}$ are the $I^{th}$ and $J^{th}$ coordinate vectors, respectively [130]. For example unit pressure along the [100] crystal direction results in a stress tensor $\sigma_{XX} = 1$, $\sigma_{YY} = \sigma_{ZZ} = \sigma_{XY} = \sigma_{XZ} = \sigma_{YZ} = 0$. This results in a shift and split of $\delta = a_1$ and $\Delta = 2b$. Similarly, for unit pressure in the [110] direction the stress tensor becomes $\sigma_{XX} = \sigma_{YY} = \sigma_{XY} = 1/2$, $\sigma_{ZZ} = \sigma_{XZ} = \sigma_{YZ} = 0$. This results in a shift and split of $\delta = a_1 + a_2$ and $\Delta = -b + c$. This simple example of changing stress direction demonstrates how all four stress susceptibility parameters are required to fully explain this interaction. Table 3.1 shows the results for uniaxial...
CHAPTER 3. DESCRIPTION OF THE NV\(^{-}\) SPIN-MECHANICAL INTERACTION

\[
\begin{array}{|c|c|c|c|}
\hline
\text{direction} & \theta & \sigma & \delta & \Delta \\
\hline
\langle 100 \rangle & 54.7^\circ & \begin{pmatrix} P & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} & a_1 & \pm 2b \\
\hline
\langle 110 \rangle & 35.2^\circ & \frac{1}{2} \begin{pmatrix} P & P & 0 \\ P & P & 0 \\ 0 & 0 & 0 \end{pmatrix} & a_1 + a_2 & \pm (b-c) \\
\hline
\langle 110 \rangle & 90.0^\circ & \frac{1}{2} \begin{pmatrix} P & -P & 0 \\ -P & P & 0 \\ 0 & 0 & 0 \end{pmatrix} & a_1 - a_2 & \pm (b+c) \\
\hline
\langle 111 \rangle & 0.0^\circ & \frac{1}{3} \begin{pmatrix} P & P & P \\ P & P & P \\ P & P & P \end{pmatrix} & a_1 + 2a_2 & - \\
\hline
\langle 1\bar{1}1 \rangle & 70.5^\circ & \frac{1}{3} \begin{pmatrix} P & -P & P \\ -P & P & -P \\ P & -P & P \end{pmatrix} & a_1 - \frac{2}{3}a_2 & \pm \frac{4}{3}c \\
\hline
\end{array}
\]

Table 3.1: Stress tensors and resulting shift (δ) and splits (∆) for all relevant uniaxial stress directions studied in this thesis. Then angle θ is between the NV axis and the uniaxial stress direction. In this table the NV direction is always \langle 111 \rangle and the stress direction is varied. This is the same as a single uniaxial stress direction and the different uniquely orientated sub-ensembles being considered.

stress along the common crystallographic directions in diamond.

3.4 Converting between stress-strain and coordinate systems

Many of the previous definitions of the NV\(^{-}\) spin-mechanical interaction have chosen to define the parameters in terms of strain in the coordinate frame of the NV centre. As such, it is important to be able to transform the spin-mechanical parameters between different coordinate systems and between stress or strain definitions. Converting the interaction between units of strain and stress requires the stiffness tensor \(C\). Changing coordinates between the NV system and the crystal system requires a rotation of both the stress or strain tensor and the stiffness tensor. Since the stiffness tensor is a fourth rank tensor, the rotation formalism is more complex. However, a single 6×6 rotation matrix (K) can be defined for rotations in the reduced Voight notation [161]. In Voight notation \(\sigma = \{\sigma_{xx}, \sigma_{yy}, \sigma_{zz}, \sigma_{yz}, \sigma_{xz}, \sigma_{xy}\}\) is a vector and the stiffness tensor \(C\) reduces to a single 6×6 matrix. This reduction simplifies the rotation formalisms to simple matrix multiplication. For tensor notation
3.4. CONVERTING BETWEEN STRESS-STRAIN AND COORDINATE SYSTEMS

\[ \sigma_{xyz} = R^T \sigma_{XYZ} R \] and for Voight notation \[ \sigma_{xyz} = K \sigma_{XYZ} \]. These transformations are described as,

\[ \sigma_{xyz} = K \sigma_{XYZ} \quad (3.13) \]
\[ \epsilon_{xyz} = (K^{-1})^T \epsilon_{XYZ} \quad (3.14) \]
\[ C_{xyz} = KC_{XYZ}K^T \quad (3.15) \]

where \( xyz, XYZ \) represent the NV and crystal coordinate systems, respectively. Following the methods in equations (3.13 - 3.15) allows the interaction to be written in either stress or strain in any coordinate system.

For example, to transform from units of stress in the crystal frame to units of strain in the NV coordinate frame. The rotation matrices \( R \) and \( K \) are defined from the transformation of \( x \leftrightarrow X : [\bar{1}\bar{1}2] \leftrightarrow [100], y \leftrightarrow Y : [\bar{1}10] \leftrightarrow [010] \) and \( z \leftrightarrow Z : [111] \leftrightarrow [001] \).

Method 1

\[ \sigma_{xyz} = C_{xyz} \epsilon_{xyz} \]
\[ \sigma_{xyz} = KC_{XYZ}K^T \epsilon_{xyz} \]
\[ \sigma_{XYZ} = K^{-1}KC_{XYZ}K^T \epsilon_{xyz} \]
\[ \sigma_{XYZ} = C_{XYZ}K^T \epsilon_{xyz} \]

Method 2

\[ \epsilon_{XYZ} = ((K^{-1})^T)^{-1} \epsilon_{xyz} \]
\[ \epsilon_{XYZ} = K^T \epsilon_{xyz} \]
\[ \sigma_{XYZ} = C_{XYZ}K^T \epsilon_{xyz} \]

Method 1 converts strain to stress in the rotated frame and then rotates the strain tensor. Method 2 rotates the strain and then converts from strain to stress in the crystal frame. Both expressions result in the spin-mechanical interaction being described as follows in terms of the stress susceptibility parameters \( (a_1, a_2, b, c) \), the non-zero components of the stiffness matrix \( (C_{11}, C_{12}, C_{44}) \) and the strain in the NV coordinate system \( (\epsilon_{xyz}) \)

\[ M_z = a_1 \left( C_{11} + 2C_{12} \right)(\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}) - 2a_2C_{44}(\epsilon_{xx} + \epsilon_{yy} - 2\epsilon_{zz}) \]
\[ M_x = \sqrt{2} \left( b(C_{11} - C_{12}) - \frac{1}{2}cC_{44} \right)2\epsilon_{xx} + (b(C_{11} - C_{12}) + cC_{44})(\epsilon_{xx} - \epsilon_{yy}) \quad (3.16) \]
\[ M_y = \sqrt{2} \left( b(C_{11} - C_{12}) - \frac{1}{2}cC_{44} \right)2\epsilon_{yz} - (b(C_{11} - C_{12}) + cC_{44})2\epsilon_{xy} \]
CHAPTER 3. DESCRIPTION OF THE NV\textsuperscript{−} SPIN-MECHANICAL INTERACTION

3.5 Conclusion

The spin-mechanical description of the NV\textsuperscript{−} centre’s spin-resonances is defined. The rotation formalisms and solid mechanics required to convert between stress and strain is outlined. These definitions are used in the next three chapters to experimentally characterise the susceptibility parameters for the NV\textsuperscript{−} spin-mechanical interaction. A comparison to previous definitions of the spin-mechanical interaction by other authors is performed. By using the full stress tensor, applying the correct rotation formalisms and changing between stress and strain using the full stiffness tensor the previous disagreement between published spin-mechanical parameters is rectified.
CHAPTER 4

Uniaxial studies and characterisation

4.1 Contributions

The experimental design, construction and execution was performed by M.S.J Barson. The data analysis was performed by M.S.J. Barson.

4.2 Introduction

Uniaxial measurements are unique in that single components of the stress tensor can easily be isolated. Combined with using differently orientated crystals, the entire stress response of the centre being investigated can be mapped. Secondly, the applied force is generally well known, so qualitative analysis does not need to rely on bending models or any other mechanical assumptions. However, due to the bulky nature of the equipment required for applying the stresses on large crystals, the use of single site optics is generally not possible. Single-site spin-mechanical measurements of NV centres within cantilevers are demonstrated in chapter 5. Nevertheless, uniaxial ensemble measurements examine the exact same spin-mechanical interaction as any other single site based measurements.

4.3 Experimental description

The uniaxial measurements were conducted using a custom built pneumatically actuated press (figure 4.1(a)). Compressive uniaxial forces were applied to opposing sides of cubic \((2 \times 2 \times 2\text{mm}^3)\) crystals via flame hardened steel anvils (56 Rockwell) with flat faces. One anvil was allowed to pivot through a cup/cone arrangement (figure 4.2(b)) to prevent any resultant moment at the crystal. The compressive force was applied from a pneumatic piston (diameter \(\sim 3\text{ in.}\)). Line pressure to the
pneumatic cylinder was from a Nitrogen gas bottle and the pressure was measured using a mechanical gauge and maintained via a gas regulator. Gas line pressures up to 300 psi were applied, which corresponds to ~2300 MPa at the crystal. The diamond cubes were exactly in the centre of the press using 3D printed sample holders that fitted into the bore of the press. The uniaxial stress ($\sigma_P$) at the crystal is determined from measuring the pneumatic cylinder pressure ($P$) and the geometry of the components in the press. The cylinder has a diameter of $d = 3$ inches $\Rightarrow A_{pis} = \pi (d/2)^2$. Since $P = F_{pis}/A_{pis} \Rightarrow F_{pis} = PA_{pis} = P\pi (d/2)^2$. The uniaxial stress at the diamond is then $\sigma_P = F_{pis}/A_{diamond} = PA_{pis}/A_{diamond}$. More experimental details about the uniaxial press and in particular about loading the diamond in the press and preventing diamond fracture are presented in appendix A.1.

The anvils in the press had to made of a very hard material so as to not deform when pushing on the diamond samples. Ferrous carbon steel was chosen as it can be machined and hardened easily. Unfortunately, this resulted in some unwanted magnetisation of the anvils, resulting in a small magnetic field at the sample. As this magnetic field produces an unwanted splitting of the NV spin resonances, an external axial nulling magnetic field was applied. The magnetic solenoid (4 G/A) was aligned axially with the piston and connected to a programmable power supply providing a controllable axial magnetic field, the maximum field used was about 20 G at the solenoid. Microwaves were generated from a Windbreak SynthNV ($P \lesssim 0$ dBm) and amplified through a 50 W amplifier. Microwaves were delivered to the sample using a two-wire transmission line that straddled either side of the crystal. The microwave wires were either terminated (50 Ω) or un-terminated.

A 532 nm 100 mW CW laser was used to optically excite the NV centres. Fluorescence was collected back through the objective lens ($f = 100$ mm achromatic), filtered (650 nm long pass) and coupled into a multimode fibre (200 µm core) to a photo-multiplier tube (PMT) detector in continuous current mode. A polarisation rotator (Fresnel rhomb type) was used to control laser polarisation. Controlling the excitation polarisation enables the signal from differently orientated sub-ensembles to be uniquely distinguished. The voltage signal from PMT was measured on a 16-bit National Instruments digital acquisition (NI DAQ) card. A simple Python Tkinter graphical user interface was developed to control and automate the experiment.

The samples were type 1b HPHT diamonds obtained from Almax-easyLabs and were prepared with polished faces of either four ⟨110⟩ faces and two ⟨100⟩ faces or two ⟨111⟩ faces and unknown other faces. The samples were irradiated with 2 MeV electrons at $5 \times 10^{17}$/cm$^2$ at the National Institutes for Quantum and Radiological Science and Technology (QST). The samples were then annealed at 570 °C in flowing
dry nitrogen gas for two hours. Infra-red absorption spectroscopy showed a single N concentration of $\sim 200$ ppm prior to annealing, this was determined by comparing the absorption coefficient of the $1130 \text{ cm}^{-1}$ peak to the data published by Kiflawi et al [162].

Uniaxial pressure measurements were conducted separately for each orientation $\langle 111 \rangle$, $\langle 110 \rangle$ and $\langle 100 \rangle$. The crystal orientations were confirmed by performing CW ODMR in an axially aligned field and noting the pattern of the ODMR spectra. For each pressure CW ODMR spectra were taken for two orthogonal excitation polarisations and multiple magnetic field values.
Figure 4.1: (a) Schematic of the uniaxial stress experiment as described in text. Note that the outer part of press that holds bottom anvil to pneumatic cylinder is not shown. (b) Photograph of diamond cube used for this experiment \((2 \times 2 \times 2 \text{ mm}^3)\), the dense ensemble of NV\(^-\) centres emit red fluorescence under excitation from the green laser. The intensity drop of the laser beam exiting the opposite face is due to the absorption of the NV\(^-\) centres.
4.4 Results and discussion

Since these measurements were conducted on a dense ensemble of NV−centres the ODMR spectra from all four differently orientated centres overlapped. The degeneracy of the $|±1\rangle$ levels is lifted from applied stress or applied magnetic field so that there is more than two distinct lines in the spectra as the interaction with the differently orientated centres is not equivalent. To isolate the signal from differently orientated centres, the polarisation of the excitation laser was modified to separate the spectra. In keeping with convention [45, 66, 130], polarisation parallel and perpendicular to the stress axis is labelled $\pi$ and $\sigma$, respectively and is shown in figure 4.3. Owing to the electric dipole selection rules of the NV centre’s optical excitation, the fluorescence intensity varies with laser polarisation as $I \propto |x \cdot \vec{E}|^2 + |y \cdot \vec{E}|^2$, where $x$ and $y$ are the coordinate directions in the NV coordinate system. A summary of the relative fluorescence intensities for different NV orientations for $\sigma$ and $\pi$ laser polarisations can be found in table 4.1.

Using table 4.1, two Lorentzian lineshapes from each ODMR spectra can easily be extracted. For example, for $\langle 111 \rangle$ stress, $\pi$ polarisation gives a signal ($S$) that is a combination of lines ($L$), $S_{\pi} = 0 \times L_{0\pi} + 8/3 L_{70\pi}$, and similarly for $\sigma$ polarisation,
CHAPTER 4. UNIAXIAL STUDIES AND CHARACTERISATION

<table>
<thead>
<tr>
<th>stress</th>
<th>$\theta$</th>
<th>#</th>
<th>$I_\sigma$</th>
<th>$I_\pi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\langle 111 \rangle$</td>
<td>0°</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>$\langle 111 \rangle$</td>
<td>70°</td>
<td>3</td>
<td>$\frac{3}{3}$</td>
<td>$\frac{3}{3}$</td>
</tr>
<tr>
<td>$\langle 110 \rangle$</td>
<td>36°</td>
<td>2</td>
<td>$\frac{2}{3}$</td>
<td>$\frac{2}{3}$</td>
</tr>
<tr>
<td>$\langle 110 \rangle$</td>
<td>90°</td>
<td>2</td>
<td>$\frac{2}{3}$</td>
<td>$\frac{2}{3}$</td>
</tr>
<tr>
<td>$\langle 100 \rangle$</td>
<td>54°</td>
<td>4</td>
<td>$\frac{4}{3}$</td>
<td>$\frac{4}{3}$</td>
</tr>
</tbody>
</table>

**Table 4.1:** Summary of centres and laser polarisation, for a given uniaxial stress direction: $\theta$ is the angle between the uniaxial stress direction and the sub-ensemble NV axis, # is the number of centres in that sub-ensemble, $I_\sigma$ and $I_\pi$ are the total signal strength when the laser polarisation is perpendicular or parallel to the stress direction, respectively. Intensity is normalised for one sub-ensemble to give a maximum of 1 fluorescence unit.

**Figure 4.3:** The orientation of unique NV sub-ensembles (blue and red) relative to the uniaxial stress direction (purple), the laser propagation direction ($k$) and the parallel ($\pi$) and perpendicular ($\sigma$) laser polarisation directions. For the case of $\langle 110 \rangle$ stress the $\sigma$ polarisation can be chosen to be either $\langle 110 \rangle$ or a $\langle 100 \rangle$, $\sigma$ was chosen in a $\langle 110 \rangle$ direction, and the laser propagating in an $\langle 100 \rangle$ direction. For the case of $\langle 111 \rangle$ stress, the exact direction of the $\sigma$ polarisation doesn’t matter, as long as it is perpendicular to $\langle 111 \rangle$. All laser polarisation directions in the perpendicular plane will give the same total emission intensity after summing over the three 70° sub-ensembles, as their orientation is equally distributed in that plane. For $\langle 100 \rangle$ the sub-ensembles are equivalently aligned relative to the applied stress, so no particular laser polarisation was required.
Figure 4.4: (a) Example of ODMR spectra from $\langle 111 \rangle$ uniaxial stress with $P \sim 2300$ MPa and $B \sim 2.4$ G in the $\langle 111 \rangle$ direction. $S_\pi$ and $S_\sigma$ denote the signals from polarisations parallel and perpendicular to the stress axis, and $L_0$ and $L_{70}$ denote the ODMR spectra contributions from centres oriented at 0° and 70° to the stress axis. (b) Example ODMR spectra for $\langle 110 \rangle$ uniaxial stress $P \sim 2300$ MPa and $B \sim 2.4$ G in the $\langle 110 \rangle$ direction.
Figure 4.5: (a), (b) Example of the centre of each line in \(\langle 111 \rangle\) and \(\langle 110 \rangle\) stress direction as the axial magnetic field generated by the coil is adjusted under an applied uniaxial stress. Each line represents a different sub-ensemble. The solid lines are a quadratic polynomial fit and the dashed lines represent the turning point value. Notice that there are a pair of lines for each orientation and that changing the field from the turning point only increases the splitting between the pairs. Also notice that the axial centres are much more sensitive to changes in the axial field, as is expected. The difference in turning point current between (a) and (b) is due to degaussing the anvils between experiments, changing the magnetisation that was nulled by the applied field. The error bars are determined from the combined fit errors using the method described in appendix B.3.
4.4. RESULTS AND DISCUSSION

\[ S_\sigma = L_0^\sigma + 5/3L_{70}^\sigma. \]

Solving such sets of equations for \( \langle 111 \rangle \) and \( \langle 110 \rangle \) in matrix form gives,

\[
\begin{pmatrix}
S_\pi \\
S_\sigma
\end{pmatrix}_{\langle 111 \rangle} =
\begin{pmatrix}
0 & 8/3 \\
1 & 5/3
\end{pmatrix}
\begin{pmatrix}
L_0^\sigma \\
L_{70}^\sigma
\end{pmatrix}
\tag{4.1}
\]

\[
\begin{pmatrix}
L_0^\sigma \\
L_{70}^\sigma
\end{pmatrix} =
\begin{pmatrix}
-5/8 & 1 \\
3/8 & 0
\end{pmatrix}
\begin{pmatrix}
S_\pi \\
S_\sigma
\end{pmatrix}_{\langle 111 \rangle}
\tag{4.2}
\]

\[
\begin{pmatrix}
S_\pi \\
S_\sigma
\end{pmatrix}_{\langle 110 \rangle} =
\begin{pmatrix}
2/3 & 2 \\
2 & 2/3
\end{pmatrix}
\begin{pmatrix}
L_{36}^\sigma \\
L_{90}^\sigma
\end{pmatrix}
\tag{4.3}
\]

\[
\begin{pmatrix}
L_{36}^\sigma \\
L_{90}^\sigma
\end{pmatrix} =
\begin{pmatrix}
-3/16 & 9/16 \\
9/16 & -3/16
\end{pmatrix}
\begin{pmatrix}
S_\pi \\
S_\sigma
\end{pmatrix}_{\langle 110 \rangle}
\tag{4.4}
\]

An example of this procedure of separating the spectra from ensembles using polarisation can be seen in figure 4.4(a). It should be noted that the this method of separating the signal using laser polarisation is determined only by the optical selection rules and doesn’t rely on consistent microwave power across separate sub-ensembles. If different sub-ensembles received differing microwave projections and as a result have different ODMR contrasts, that would be reproduced by the above extraction method. The microwave polarisation \( \vec{B}_0 \) produced from our two-wire transmission line is inhomogeneous over the optical excitation volume but on average roughly parallel to the stress and magnetic field direction. This inhomogeneity ensures that all sub-ensembles receive at least some non-negligible microwave excitation. Since only the location of the central frequency of each spin-resonance is required any difference in contrast between separate lineshapes is of no consequence. The ODMR spectral lineshapes were fitted as Lorentzians using a custom least squares method optimised with the bounded sequential least squares programming (SLSQP) algorithm from the SciPy library, details in appendix B.3.

The magnetic field was swept through strengths that opposed the inherent magnetisation of the anvils so a turning point in the magnetic splitting could be obtained. No nulling was applied to any transverse magnetisation of the anvils but the anvils were systematically degaussed so only an axial net magnetisation was present. Since the magnetic interaction will only split the resonances further apart and not shift them, if a turning point in the splitting due to sweeping an applied field can be found, then it is known that this remaining splitting and shift is due to the applied stress interaction only. Example behaviour is shown in figure 4.5(a). Interestingly, the magnetisation of the anvils was not consistent with pressure. This is thought to
Figure 4.6: (a-b) Stress shift and splitting of ODMR spectra for ⟨111⟩ oriented uniaxial stress. The two possible sub-ensembles are orientated either at 0° or 70° to the uniaxial stress direction. The error bars are determined from the combined fit errors using the method described in appendix B.3.

be due to change in the ferromagnetic structure of the steel at high pressures and for this reason a nulling field sweep was applied at every pressure increment. Using the turning point line position as the ‘true’ value due to stress only, the behaviour of the energy levels due to changes in applied stress can be observed.

The shift and split behaviour of the ODMR spectra is shown in figures 4.6, 4.7, 4.8 and summarised in table 4.2. These values lead to the stress susceptibility parameters show in table 4.3. Disagreement between the ⟨110⟩ and ⟨111⟩ orientations is due to misalignment from the polishing of the ⟨111⟩ sample. This polishing error is expected as the ⟨111⟩ direction of diamond is the hardest direction [163] and cannot be polished precisely to a ⟨111⟩ direction. This misalignment was determined by working backwards by applying a rotation matrix \( R(\theta, \phi) \) to the ⟨111⟩ uniaxial stress tensor and optimising the angles until extracted stress parameters agree with the ⟨110⟩ parameters. This process yields angles of \( (\theta, \phi) = (11.0^\circ, 2.98^\circ) \), this gives
Figure 4.7: (a-b) Stress shift and splitting of ODMR spectra for $\langle 110 \rangle$ oriented uniaxial stress. The two possible sub-ensembles are orientated either 90° or 36° to the uniaxial stress direction. The error bars are determined from the combined fit errors using the method described in appendix B.3.
Figure 4.8: (a-b) Stress shift and splitting of ODMR spectra for \( \langle 100 \rangle \) oriented uniaxial stress. The four possible sub-ensembles are equivalently orientated at 54° to the uniaxial stress direction. The error bars are determined from the combined fit errors using the method described in appendix B.3.
a polishing face angle of approximately $3^\circ$. The angle $\theta \sim 11^\circ$ is a rotation of the stress tensor about the $\langle 111 \rangle$ direction and does not represent a misalignment of the $\langle 111 \rangle$ diamond face. This is important since this misalignment ($\phi$) can tilt towards directions that are a linear combination of $\langle 100 \rangle$ or $\langle 110 \rangle$ and stresses in those directions do not have equal spin-mechanical responses. The $3^\circ$ value agrees with the normally achieved mechanical polishing error.\footnote{Presentation by Prof Jan Meijer (Universität Leipzig) at the 2016 DIADEMS workshop in Cargèse, Corsica. Corroborated by private discussion with Prof Mark Newton (Warwick University)} For this reason the $\langle 110 \rangle$ parameters are used to determine the spin-mechanical parameters. However, the $\langle 111 \rangle$ results still show very good functional agreement with our model.

As shown in figure 4.8, the $\langle 100 \rangle$ did not show a linear splitting of spin resonance with increasing stress. This can be explained if there is an inherent crystal stress already present in the crystal which opposes the applied stress in this direction, that is $\langle 100 \rangle$ but in the other direction. For example, if the stress tensor is $\sigma = \sigma_{\text{inh}} + \sigma_{\text{app}}$, gives the interaction $\mathcal{M}_{\text{inh}} + \mathcal{M}_{\text{app}}$, this would give a shift of the spin-resonances of

$$\Delta = \sqrt{(\Delta \mathcal{M}_{\text{inh}} + \mathcal{M}_{\text{app}})^2 + (\Delta \mathcal{M}_{\text{app}} + \mathcal{M}_{\text{inh}})^2}.$$  

\begin{equation}
\Delta = \sqrt{(\Delta \mathcal{M}_{\text{inh}} + \Delta \mathcal{M}_{\text{app}})^2 + 2(\Delta \mathcal{M}_{\text{inh}} \mathcal{M}_{\text{app}} + \Delta \mathcal{M}_{\text{app}} \mathcal{M}_{\text{inh}})}.
\end{equation}

Once the applied stress was larger than the inherent stress ($\sigma_{\text{inh}} < \sigma_{\text{app}}$) then the spin response would start to exhibit the linear behaviour shown in the other stress orientations. Due to this uncertainty, the $\langle 100 \rangle$ data was not included in the determination of the susceptibility parameters. This inherent stress is interesting as it is common for ensemble ODMR measurements at zero magnetic field to have a slightly split ODMR spectra (1-10 MHz). This is often assumed to be due to some strain present in the crystal. Our uniaxial analysis shows that the stress ODMR splitting is of order roughly 5 MHz/GPa. For this assumption to be true these crystals should have internal stresses of order 1 GPa, which is high but consistent with single crystals of similar nitrogen concentration [164]. It would be interesting to perform a census of the inherent zero-field splitting in different diamonds with NV ensembles and to determine if the internal stresses are dependent on crystal type and impurity density etc, and if assigning zero-field splitting to crystal strain is valid. Future studies could use the stress susceptibilities we have determined here for investigations and modelling of the inherent internal strain of ensemble samples from implantation, irradiation or growth. This could be extended to wide-field imaging of the inherent strain throughout a crystal to get a better understanding of
CHAPTER 4. UNIAXIAL STUDIES AND CHARACTERISATION

Sub-ensemble | Energy | Shift $\delta$ (MHz/GPa) | Split $\Delta$ (MHz/GPa)
--- | --- | --- | ---
$\langle 111 \rangle_{0^\circ}$ | $a_1 + 2a_2$ | $-2.3 \pm 0.1$ | $0.8 \pm 0.2$
$\langle 111 \rangle_{70^\circ}$ | $a_1 - \frac{2}{3}a_2 \pm \frac{2}{3}c$ | $6.20 \pm 0.04$ | $2.63 \pm 0.06$
$\langle 110 \rangle_{90^\circ}$ | $a_1 - a_2 \pm (b + c)$ | $8.1 \pm 0.7$ | $1.3 \pm 1.2$
$\langle 110 \rangle_{36^\circ}$ | $a_1 + a_2 \pm (b - c)$ | $0.5 \pm 0.1$ | $5.4 \pm 0.2$

Table 4.2: Shift and splits of the spin resonance for sub-ensembles in samples with uniaxial stress aligned along the $\langle 111 \rangle$ and $\langle 110 \rangle$ directions.

orientation | $a_1$ (MHz/GPa) | $a_2$ (MHz/GPa) | $b$ (MHz/GPa) | $c$ (MHz/GPa)
--- | --- | --- | --- | ---
$\langle 111 \rangle$ | $4.08 \pm 0.04$ | $-3.17 \pm 0.05$ | - | $1.97 \pm 0.05$
$\langle 110 \rangle$ | $4.38 \pm 0.2$ | $-3.74 \pm 0.2$ | $-0.80 \pm 0.3$ | $2.17 \pm 0.4$

Table 4.3: Stress susceptibility parameters for uniaxial stress aligned along the $\langle 111 \rangle$ and $\langle 110 \rangle$ directions.

There have been several recent investigations into the NV centre’s spin-mechanical interaction, including hydrostatic [32], AC [33, 34, 35, 36, 37, 38] and DC strain couplings [33]. Apart from the hydrostatic study, all other publications incorporate just one perpendicular and one parallel susceptibility parameter in their definition of the spin-mechanical interaction, where parallel and perpendicular indicate the strain or stress that is aligned or transverse to the NV axis. This two parameter description can phenomenologically describe the observed shifting and/or splitting of the spin resonances in these prior works. However, as demonstrated above, due to the trigonal symmetry of the NV centre and the cubic nature of diamond, the two parameters obtained from these works can not fully describe the interaction for another stress/strain direction, even taking into account the appropriate coordinate transformations. This means that results that were determined in these particular experiments may not match other experiments unless the exact same crystal stress was applied, possibly explaining disagreement in the literature [34, 33].

4.5 Comparison to previous definitions of the spin-mechanical interaction

The need for more than two parameters can be further reasoned by considering the crystal environment around the NV centre. Using a single perpendicular parameter implies that the mechanical environment in all directions perpendicular from the defect axis are universally similar for all NV centre orientations. Similarly
for the axial direction. The cubic symmetry of the diamond implies there are three unique crystal directions, which gives rise to directionally different material properties (strength, stiffness, heat conduction, thermal expansion etc). Since there can be no single perpendicular or axial direction from a trigonal defect that matches one unique cubic crystal direction there cannot be a single term that defines this coupling. The four parameters \((a_1, a_2, b, c)\) previously defined, are the minimum number of parameters required by arguments of symmetry to describe this interaction \([57, 130]\). Another complication arising from the cubic nature of diamond is the relatively strong anisotropic mechanical behaviour (Zener anisotropy ratio \(A = 2.3\)). This means that assumptions of isotropic mechanics such as the use of a the Poisson ratio for shear modulus \((2(1 + \nu)/E \neq G)\) or neglecting shear effects \([34, 33]\) have to be treated with care.

This difference in assumptions makes it difficult to compare the stress susceptibility parameters from other publications, particularly the neglect of the shear strain component \([33, 34]\) (e.g. \(\epsilon_{xz}\)) as this generally contributes to the splitting terms of the spin resonance \((M_x, M_y)\). Ovartchaiyapong et al \([34]\) defined the interaction in terms of the strain components of the NV axis, they used a microcantilever that generated bending stress in the direction of the \((110)\) cantilever. For a unit uniaxial stress in the \((110)\) direction, the stress tensor becomes \(\sigma_{XX} = \sigma_{YY} = \sigma_{XY} = 1/2, \sigma_{ZZ} = \sigma_{XZ} = \sigma_{YZ} = 0\). The strain tensor in the NV coordinate system can be defined in terms of the stress tensor in the crystal coordinate system using \(\epsilon_{xyz} = (K^{-1})^T C_{XYZ}^{-1} \sigma_{XYZ}\), which gives the strain response from the unit uniaxial \((110)\) stress in Voigt notation as \(\epsilon_{xyz} = \{2.2, -0.04, 5.4, 0, 9.1, 0\} \times 10^{-13}\), where the stiffness matrix terms \(\{C_{11}, C_{12}, C_{44}\} = \{1076, 125, 576\}\) GPa were used \([165]\). Following Ovartchaiyapong et al’s definition, the axial strain \(\epsilon_{zz}\) gives rise to a shift of the spin resonance \(\delta = d|| \epsilon_{zz}\), where \(d|| = 13.4 \pm 0.4\) GHz/strain. This gives the shift \(\delta = 13.3\) (GHz/strain) \(\times 5.4 \times 10^{-13}\) (strain/Pa) = 7.3 \pm 0.4 MHz/GPa which agrees relatively well with our \(a_1 - a_2 = 8.1 \pm 0.3\) MHz/GPa (a difference of 0.8 \pm 0.5). However, there is no agreement to the splitting term \(\Delta\), as they did not include shear strain terms in the definition of the spin-mechanical interaction and these terms are large with the unit stress in the \((110)\) direction giving a shear strain \(\epsilon_{xz} = 9.1 \times 10^{-13}\) larger than all other terms in the strain tensor.

Teissier et al \([33]\) performed similar measurements using a microcantilever cut along the \((100)\) direction and also defined their interaction in terms of the strain in the NV coordinate system. For a unit stress in the \((100)\) direction the stress tensor becomes \(\sigma_{XX} = 1, \sigma_{YY} = \sigma_{ZZ} = \sigma_{XY} = \sigma_{XZ} = \sigma_{YZ} = 0\). Using the same relation as before \(\epsilon_{xyz} = (K^{-1})^T C_{XYZ}^{-1} \sigma_{XYZ}\) gives a strain tensor \(\epsilon_{xyz} =
\( \{0.7, 4.3, 2.5, -8.7, 5.0, -6.\} \times 10^{-13} \) and using their method we get a shift \( \delta = d_\parallel \epsilon_{zz} \), where \( d_\parallel = 5.46 \pm 0.31 \) GHz. This gives a shift of \( \delta = 5.47 \) GHz/strain \( \times 2.5 \times 10^{-13} \) strain/Pa = 1.4 MHz/GPa three times less than expected from our result \( \delta = a_1 = 4.4 \) MHz/GPa. This is due to the incorrect assignment of the strain tensor in the NV coordinate system from the strain in cantilever coordinates. Teissier et al state, that the axial strain \( \epsilon_z \) and transverse strain \( \epsilon_{x,y} \) are \( \sqrt{2/3} \epsilon^{[100]} \) and \( \sqrt{1/3} \epsilon^{[100]} \), respectively, where \( \epsilon^{[100]} \) is the strain along the cantilever due to the cantilever bending. This is incorrect because strain rotationally transforms as a tensor not a vector and more formal rotation processes are required (as shown in section 3.4). However, their spectra and results look very promising. Using their strain relationship \( \epsilon^{[100]} = \alpha \kappa \), where \( \alpha = 7 \times 10^{-4} / \mu \)m and \( \kappa \) is the cantilever displacement, the uniaxial bending stress can be found as \( \sigma_{XX} = C_{11} \epsilon^{[100]} = C_{11} \alpha \kappa \). Working backwards from their expression for the shift \( \delta = d_\parallel \epsilon_z = d_\parallel \sqrt{2/3} \epsilon^{[100]} = d_\parallel \sqrt{2/3} \alpha \kappa \). The shift per stress is then

\[
\frac{\delta}{\sigma_{XX}} = \frac{d_\parallel \sqrt{2/3} \alpha \kappa}{C_{11} \alpha \kappa} = \frac{5.46 \text{ GHz} \times \sqrt{2/3}}{1076 \text{ GPa}} = 4.2 \pm 0.2 \text{ MHz/GPa},
\]

which agrees well with our result of \( \delta = a_1 = 4.4 \pm 0.2 \) MHz/GPa. (a difference of 0.2 \pm 0.3 MHz/GPa).

### 4.6 Conclusion

The spin-mechanical susceptibility parameters determined in this chapter, together with their agreement and unification of previous spin-mechanical descriptions demonstrate a robust and unambiguous description of the spin-mechanical interaction. This agreement also highlights that this interaction is intrinsic to the NV centre and can be applied to multiple samples and NV centres for useful metrology generally. Using the values determined in this chapter, the next chapters demonstrate useful force measurements using this interaction and expand on other potential metrology using NV centres.
CHAPTER 5

Force sensing using diamond cantilevers

5.1 Contributions

The experimental design, construction and execution was performed by M.S.J. Barson and P. Peddibhotla with additional help from L. McGuinness and F. Jelezko. The cantilevers were manufactured by O. Freydin, K. Ganesan, P. Ovartchaiyapong and A.C. Bleszynski Jayich. The data analysis was performed by M.S.J. Barson.

5.2 Introduction

To test the application and understanding of the spin-mechanical interaction at the micro-scale, an experiment that measured the interaction with single NV centres was desired. One way of doing this is to measure the applied bending stresses in diamond cantilevers with NV centres within the cantilever. Cantilevers were chosen over other mechanical elements due to their ease of manufacturing, the large bending stresses that can be generated and the easy optical access to image single NV centres.

5.3 Diamond cantilever fabrication

Cantilevers were created in single crystal diamond using focussed-ion beam (FIB) milling at the University of Melbourne with O. Freydin and K. Ganesan. These FIB milled cantilevers exhibited a large amount of fluorescence due to neutral vacancy centres (GR1) that were seemingly produced during the milling process, as shown in figure 5.1(a). There was no GR1 fluorescence at locations away from where the FIB milling was performed, just conventional NV$^-$ fluorescence as shown in figure 5.1(b). This large background fluorescence from the GR1 is undesired because it reduces the optical ODMR contrast and achievable sensitivity. It may have been
possible to anneal the vacancies out of the diamond, however, the vacancies would be trapped at nearby nitrogen [45] potentially increasing the density of NV centres beyond resolvable single sites. There was also a appreciable (∼2×) increase in the density of NV centres at the FIB milling site from NV creation as vacancies were generated. It became clear that FIB milling was not the appropriate method to produce these cantilevers.

An alternative method used to fabricate these structures is lithography and reactive ion-etching [42, 166, 167]. These processes involve carefully determined etching recipes to generate very uniform and smooth surfaces. Our collaborators at Melbourne University pursued these methods successfully [168], unfortunately not within the time frame of these measurements. Fortunately suitable diamond cantilever samples were obtained on loan from our collaborators Ovartchaiyapong et al at the University of California, Santa Barbara.

5.4 Experimental description

Single defects in the diamond cantilevers were measured using a custom built scanning confocal microscope, shown in figure 5.2(a). The sample was placed over a 0.95 NA air objective mounted on a piezo scanner. The excitation was provided by a Laser Quantum 500mW GEM laser providing approximately 0.1-3.0 mW at the objective. Laser polarisation could be rotated using a half wave plate (HWP), allowing for determination of the NV centre orientations within the sample. Fluorescence was collected through 25 µm pin hole onto a Perkin-Elmer single photon avalanche diode (SPAD). Microwaves were provided by a Rohde & Schwarz SMIQ frequency
5.4. EXPERIMENTAL DESCRIPTION

Figure 5.2: (a) Schematic of confocal system. (b) Model of cantilever with objective and tungsten tip. The NV centres studied were at the base of the cantilever where the greatest bending stress occurs.

generator amplified using an Amplifier Research 50 W amplifier into a 25 µm wire soldered near the base of the cantilevers. The samples were mounted on a printed circuit board (PCB) which contains a transmission line to which the microwave wire is soldered. The tip of the cantilevers were displaced using a tungsten tip mounted on a Thorlabs stepper motor stage with 29 nm step resolution. The cantilevers could also be displaced using a home built AFM system that could be mounted on top of the sample. The tungsten tip and stepper motor were positioned above the diamond cantilever using a manual micrometer stage. A camera and the confocal back reflection were used as a guide to place the tungsten point at the tip of the diamond cantilever. No magnetic fields were applied to the sample. The sample preparation and processing is the same as outlined in Ovartchaiyapong et al [34].

Single NV centres were measured at the base of the cantilevers using the confocal microscope (figure 5.3(b)). However, optical spin contrast was low (< 10%) possibly due to some unknown high background fluorescence in the sample. A spectrometer was not available with the confocal microscope used for this experiment, so the source of this background fluorescence is not precisely known. The background was still lower than what was seen in the FIB samples, in which no single NVs could be seen. The low contrast was not attributed to low microwave power as de-polarising the spin with a large magnetic field yielded the same optical contrast. This poor
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contrast meant that there was difficulty in pursuing pulsed measurements (Rabi, Ramsey, Hahn-echo etc) as very long signal integrating was required for the low contrast signal to beat the shot noise. However, CW ODMR measurements were possible, in particular pulsed ODMR measurements were used to limit power broadening. In this measurement microwave $\pi$ pulses are performed followed by an optical read out pulse, but microwave frequency is continuously swept to build an ODMR spectra [95]. These pulsed ODMR measurements resolved the nitrogen hyperfine peaks within the $|\pm 1\rangle$ levels and as such our fitting had sub-MHz uncertainty.

The deflection of the beam was measured optically using the confocal microscope by performing scans along and through the thin diamond cantilever ($x-z$ slices) as shown in figure 5.4(a). The thickness of the cantilever ($\sim 500$ nm) is approximately diffraction limited but the cantilever $z-$position can determined more precisely by fitting a Gaussian to the intensity of the confocal image in slices. This allows for determination of the centre of the cantilever at each $x$ position within approximately $50$ nm in $z$. A Gaussian function was used as this approximates the point spread function of the confocal microscope. Due to a small tilt ($\sim 3^\circ$) of the sample relative to the microscope, the extracted cantilever $(x,z)$ coordinates had to be rotated. This was achieved by fitting a cubic polynomial $z(x) = ax^3 + bx^2 + cx + d$ to the shape of the cantilever and rotating such that base of the beam had a gradient $z'(x = 0) = 0$. This is enforced by rotating the coordinates in the opposite direction the value of $\beta = -c$ using the matrix,

$$ R = \begin{pmatrix} \frac{1}{\sqrt{1+\beta^2}} & -\beta \\ \beta \frac{1}{\sqrt{1+\beta^2}} & \frac{1}{\sqrt{1+\beta^2}} \end{pmatrix} \quad (5.1) $$

$$ \begin{pmatrix} x' \\ z' \end{pmatrix} = R \begin{pmatrix} x \\ z \end{pmatrix} \quad (5.2) $$

This was done, to prepare the $(x,z)$ cantilever position data to the form required for fitting equation (5.3).
5.4. EXPERIMENTAL DESCRIPTION

Figure 5.3: (a) Microscope image where the particular cantilever that was used is highlighted in red. (b) Confocal map of NV centres at base of cantilever with one particular NV that was measured circled. Variation in brightness is due to sample tilt relative to the microscope. The zoomed in region is represented by the box on the lower image.
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Figure 5.4: Example $x - z$ confocal scan of deflected cantilever, the red line shows the centre of a Gaussian function that was fitted in the $z$ direction for each $x$ point. The image has not been rotated.

5.5 Results and discussion

The resulting deflection shapes of the diamond cantilever can be compared to elastic beam theory to obtain a prediction for the force exerted by the tungsten tip (figure 5.7). The shapes were fitted using the following Euler-Bernoulli expression for a uniform cantilever with a point load at the tip. As shown in figure 5.5, the bending moment is simply $M(x) = F(L - x)$, and the associated deflection can be found by integrating $EI \frac{dz(x)}{dx} = -M(x)$ and using the boundary conditions $z'(0) = z(0) = 0$, resulting in the expression

$$z(x) = \frac{F_{E-B}x^2}{6EI} (3L - x). \tag{5.3}$$

The force $F_{E-B}$ was the only free parameter in the fitting procedure. The method of fitting the entire shape of the deflected cantilever, gave much better precision in $F_{E-B}$ than just using a single deflection measurement of the tip and considering the force due to the linear spring constant $k = F/\Delta z = Ewt^3/4L^3$.

The force from the ODMR measurements is determined by

$$F_{ODMR} = \frac{\delta}{(a_1 - a_2) \xi_x(L - \xi_x)} \frac{I}{\xi_z} \tag{5.4}$$

This is simply due to the ODMR shift bending stress dependence $\delta = \sigma(a_1 - a_2)$ for this $\langle 110 \rangle$ aligned cantilever and the bending stress in a cantilever due to a point load. As shown in figure 5.5, the bending moment is $M = F\xi_x$, and the
5.5. RESULTS AND DISCUSSION

Figure 5.5: Euler-Bernoulli derivation of the deflection of a cantilever subject to a point load \(F\) at the tip. (a) is a free-body-diagram of the forces acting on the cantilever, applying Newton’s laws the resultant force \(R = F\) and the resultant moment \(M = FL\). (b) is the shear \((V)\) developed in the beam due to bending. (c) is the bending moment \((M)\) developed in the beam due to the bending. (d) is the resulting deflected shape \((z(x))\) of the cantilever due to the force \(F\). (e) shows the bending \((\sigma_B)\) and shear stress \((\sigma_V)\) developed inside the beam [169].
Figure 5.6: (a) Position $\vec{\xi} = (\xi_x, \xi_y, \xi_z)$ of the NV within the cantilever, the coordinate origin is defined as the centre of the base of the cantilever. Inset shows the orientations of the carbon bonds for a $\langle 110 \rangle$ cut sample. The possible NV orientations are either 90° or 36° about the $x$ axis relative to the $z$ axis. The bending stress at the surface of the cantilever will be along the axial $x$ direction. (b) Polarisation dependence of two NV centres in the cantilever. Since the two fluorescence signals have opposite phase, the two NV centres are orthogonal from the perspective of the laser incident onto the bottom surface of the cantilever. This proves that the bottom surface is a $\langle 100 \rangle$ face. Furthermore, since the NV centres are at a maximum/minimum at 0° when the laser polarisation is orthogonal to the cantilever axis, the NV centres are perpendicular/parallel to the cantilever axis. This proves that the cantilever axis is a $\langle 110 \rangle$ direction. Note that waveplate angle $= \theta/2$. The inset demonstrates the laser polarisation angle relative to the $\langle 100 \rangle$ face which has been chosen to have $\langle 110 \rangle$ in the $x$ direction.
bending stress is \( \sigma = M \xi_z / I \). Where \((\xi_x, \xi_z)\) is the location of the NV centre in the cantilever, as shown in figure 5.6(a). The mechanics of bending is shown in more detail in chapter 6. The bending stress is along the \((110)\) longitudinal axis of the cantilever, which is perpendicular to the NV centre’s orientation (confirmed via polarisation measurements, figure 5.6(b)). The position of the NV centre from the neutral axis in the \(y\) direction was ignored as the load was centrally placed at the tip of the cantilever. Even so, if a non-central loading creates a twisting bending stress in the cantilever about the \(x\) axis, the aspect ratio of the cantilever ensures that transverse \((t)\) bending stresses would be negligible compared to axial \((a)\) bending stress. This is because the beam \((w \times t \times L = 11 \times 0.58 \times 200 \mu m^3)\) is much longer than it is wide \(L/(w/2) > 40\), therefore, the bending transverse bending moment is much smaller than the axial bending moment \(M_a/M_t > 40\). Consequently the bending stresses show the same behaviour \(\sigma_a/\sigma_t > 40\).

Shear stress was neglected because (1) the NV was close to the surface and the shear stress depends quadratically on distance from the neutral axis. And (2) at the base of the cantilever the bending stress is much larger than the shear stress, which is independent of \(x\) position within cantilever. Using the descriptions shown in figure 5.5, the shear stress is \(\sigma_V = V ((h/2)^2 - \xi_z^2) / 2I\) and the bending stress is \(\sigma_B = M \xi_z / I\). For a rectangular cantilever with a point load \(F\) the bending moment \(M = F(L - \xi_z)\) and the shear is constant throughout the beam \(V = F\). Therefore the ratio of bending stress to shear stress \(\sigma_B/\sigma_V = 2L \xi_z / ((h/2)^2 - \xi_z^2)\). For the
measured NV position of \((\xi_x, \xi_z) = (5.4 \mu m, 0.02 \mu m)\) and cantilever dimensions of \(w \times t \times L = 11 \times 0.58 \times 200 \mu m^3\) this ratio is \(\sigma_B/\sigma_v > 6 \times 10^3\), demonstrating that near the surface of the base of a long cantilever the shear stress is negligible in comparison to the bending stress.

The \(\xi_x\) position was determined from the confocal imaging as 5.4 \(\mu m\) from the base of the cantilever and the depth \((\xi_z)\) was estimated to be 20 \(\pm\) 7 nm from the implantation energy using SRIM simulation software [34]. The cantilever shape and size was determined using the confocal microscope, it was rectangular in shape with a width of the 10 \(\mu m\) \(\pm\) 0.1 \(\mu m\) and length of 200 \(\mu m\) \(\pm\) 0.1 \(\mu m\). The \(x-y\) cantilever size and NV centre \((x, y)\) location can be very accurately determined from the confocal imaging and integrating over multiple images gives an uncertainty of approximately \(\pm 0.1 \mu m\). The uncertainty in the thickness of the cantilever was determined from the standard error in the mean thickness from the beam shape Gaussian fitting procedure, yielding a thickness of 0.58 \(\pm\) 0.02 \(\mu m\). Even though the thickness is only twice the diffraction limit of the confocal microscope (\(\sim 300\) nm), over 1600 Gaussian fits were performed on the cantilever thickness in the determining the bent cantilever shape allowing for quite a statistically accurate measurement of the thickness. In future studies for optimised force sensing devices, the thickness could be determined more systematically using an AFM/SEM measurement of the cantilevers. By far the largest uncertainty for the force measurement is in the depth of the NV centre. This depth location can be more sensitively \((\lesssim 1 \text{nm})\) determined by spin-resonance magnetometry ranging techniques [170, 171]. Due to time constraints and the previously mentioned difficulty in finding suitable NV\(^-\) centres only one cantilever was measured in detail.

The final comparison of \(F_{E-B}\) and \(F_{ODMR}\) in figure 5.9(a) show excellent agreement. This demonstrates that the macroscopic Euler-Bernoulli interpretation of the bending mechanics is applicable and accurate at the nanoscale. This also demonstrates that the characterisation of the spin-mechanical interaction using uniaxial measurements on dense ensembles gives very good agreement to this single-site experiment. This confirms that the spin-mechanical parameters we have determined are intrinsic to the NV\(^-\) centre itself and not somehow sample dependent. This result also demonstrates that the NV\(^-\) centre can be a useful and sensitive force sensor, allowing for fundamentally new force sensing technology based on spin-mechanical interactions.
5.5. RESULTS AND DISCUSSION

Figure 5.8: ODMR spectra of the same NV centre for 2 $\mu$m (upper) and 40 $\mu$m (lower) tip deflection. The nature of the hyperfine peaks is not clear. The spacing of the hyperfine peaks is consistent with the $^{14}$N hyperfine interaction. However, there are more peaks than expected for a single NV$^{-14}$N hyperfine spectra. The spectra is consistent with the addition of a nearby $^{13}$C spin that gives a zero-field splitting of 6.4 MHz. Interactions of such strength from a nearby $^{13}$C are commonly encountered [92]. The spectra was consistent and repeatable for all stress values. There was no apparent splitting of the lines relative to each other, just a mean shift, which is consistent with compressive stress in the $\langle 110 \rangle$ for a $36^\circ$ aligned centre, as shown in figure 4.7.
5.6 Force measurement sensitivity

To compare the force sensitivity of previous cantilever measurements obtained by measuring ODMR spectra to the generalised shot noise expression in section 2.1.3, the sensitivity per frequency point of the ODMR spectra was considered. Assuming shot-noise limited detection, this sensitivity is

$$\eta_{DC} = \Delta F_{ODMR} / \sqrt{T/n} \sim 29 \text{ nN Hz}^{-1/2}$$

where \(\Delta F_{ODMR} = 29 \text{nN}\) is the average force uncertainty obtained from a complete spectrum, \(T = 12 \text{ minutes}\) is the total spectrum integration time and \(n = 400\) is the number of frequency points. Note that \(T/n\) is the measurement time per frequency point. This experiment was designed as a proof of principle demonstration of the force measurement capability of the NV\(^-\) centre and the extension of solid mechanics and spin-mechanical model to the microscale. As such, the experiment and sample were far from optimised for force sensitivity. In particular, (1) for the pulsed ODMR measurement, the photon counting was not gated, so averaging times were long as significant number of useless photons were included in the detection; (2) the sample had very poor ODMR optical contrast (< 10%) which reduces the signal clarity; and (3) the geometry of the device could be made to generate a higher bending stress for a given force.
Consider a more ideal measurement with a cylindrical cantilever of length $L = 1\mu m$ and diameter $d = 100\, nm$. The greatest bending stress is developed at the base of the cantilever with a transverse force $F$ at the tip of the cantilever. The bending stress on the surface at the base of the cantilever is $\sigma = FLd/2I$, where $I = \pi d^4/64$.

For a cantilever orientated in the $\langle 100 \rangle$ direction, the bending stress will also be in a $\langle 100 \rangle$ direction, with a maximum change in spin resonance of $a_1 - 2b = 10.1\, MHz/GPa\, (b < 0)$. Combining these two expressions gives the change in spin-resonance per unit force

$$\frac{d\Delta f}{dF} = \frac{d\Delta f}{d\sigma} \frac{d\sigma}{dF} = (a_1 - 2b) \frac{Ld}{2I}$$

$$= 10.1 \times 10^{-3} \left[ \frac{Hz}{N/m^2} \right] \times \frac{1 \times 10^{-6} [m] \times 100 \times 10^{-9} [m]}{\pi \times (100 \times 10^{-9})^4/64 [m^4]}$$

$$\approx 100\, MHz/\mu N.$$

Inserting this into equation (2.7) gives the sensitivity

$$\eta_{DC(AC)} = \left(2\pi K \frac{d\Delta f_{mech}}{dF} \sqrt{T_{DC(AC)}}\right)^{-1},$$

where $K \approx 0.01$ is the typical value of the factor that accounts for the finite ODMR contrast and photon count rate and detection, and $T_{DC(AC)}$ is the time it takes to perform each measurement shot of the relevant quantum sensing technique. The simplest DC and AC techniques are Ramsey and Hahn-echo, respectively, where $T_{DC} \leq T_2^* \approx 10\, \mu s$ and $T_{AC} \leq T_2 \approx 100\, \mu s$ are realistic values for NV centres in nano-structures [15, 172]. The resulting optimal force sensitivity is $30\, pN/\sqrt{Hz}$ for AC and $50\, pN/\sqrt{Hz}$ for DC force sensing.

This more optimal sensitivity is a factor of $\sim 500$ larger than obtained from the cantilever measurement. A factor of $4hab^2/\pi w^2l \sim 18$ reduction in sensitivity can explained by the difference in geometry, where $(w, h)$ are the nanopillar dimensions and $a = 11\, \mu m$, $b = 0.5\, \mu m$ and $l = 200\, \mu m$ are the width, thickness and length of the cantilever, respectively. The remaining factor of $\sim 26$ is almost completely accounted for by the reduced ODMR contrast ($< 10\%$), low count rate due to our objective ($\sim 20\, kcounts/s$) and the non-gated photon detection in our pulsed ODMR measurements (combine to give a $K \sim 2 \times 10^{-4}$) and the difference in spin-mechanical susceptibilities ($(a_1 - a_2)/(a_1 - 2b) \sim 1.25$). This shows that given the far from ideal experimental conditions obtained, the optimal estimate of the sensitivity and the
Figure 5.10: Comparison of the size/spatial resolution (points) and range (indicated by connecting lines) of detectable DC forces of individual NSMS nanopillars (red)/nanopillar arrays (red), the diamond microcantilever measured in this work (orange), and existing techniques (blue) for point-wise force sensing/imaging (green). The values for existing techniques were collected from refs [173, 174, 175].

Achieved cantilever measurement sensitivities are in relatively good agreement.

Given this optimal sensitivity value, figure 5.10 compares this NV DC force sensitivity and sensor size to other comparable technologies. It is clear that nano-spin-mechanical sensors (NSMS) using NV centres in diamond do not have a sensitivity greater than atomic force microscopy or optical tweezers. NSMS devices however, can be made into very small size sensors, which is important for sensing intracellular forces [173] and high density force imaging. Novel force sensing methods using NV centres are discussed in the next chapter.

5.6.1 Comparison with alternate NV$^-$ force sensing techniques

To compare alternate methods in which forces could be detected with NV$^-$ NSMS devices, three alternate sensing methods are considered for a single diamond nanopillar. The three sensing methods compared are (1) measuring the change in the spin resonance due to the spin-mechanical interaction, (2) optical detection of the deflection of the nanopillar tip; and (3) measuring the shift of the spin resonance due to a magnetic field gradient.

For a simple cylindrical nanopillar of height $h$ and width $w$ aligned in a [001] direction (figure 5.11(a)), a transverse force $\vec{F}$ exerted at the tip will result in bending throughout the nanopillar. Using simple Euler-Bernoulli beam theory the displacement of the tip is $\vec{r}_{tip}(\vec{F}) = \frac{h^3}{3} \frac{\vec{F}}{EI}$ and the bending stress at the NV caused
by this displacement is $\sigma_{ZZ}(\vec{F}) = h \vec{F} \cdot \vec{\xi} / I$. Where $E = 1220 \text{ GPa}$ is the Young’s modulus of diamond and $I = \pi w^4 / 64$ is second moment of area of the nanopillar and $\vec{\xi}$ are the internal coordinates of the NV with respect the central axis of the nanopillar (XYZ). The spin-mechanical shift of the spin resonance of this NV is $\Delta f_{\pm}^{\text{mech}} = (a_1 \pm 2b) \sigma_{ZZ}(\vec{F})$. For an example design of $w = 100 \text{ nm}$ and $h = 1 \mu \text{m}$ the spin-mechanical force sensitivity is $\eta \sim 50 \text{ pN}/\sqrt{\text{Hz}}$. However, if the displacement of the tip is determined optically using conventional diffraction limited optics with a minimum resolution of $\sim 250 \text{ nm}$ then the minimum resolvable force would be $\sim 4.5 \mu \text{N}$. Additionally, measuring absolute displacements optically is challenging due to from thermal drifts of the optical stage at the nm length scale.

To beat the limitation of larger than diffraction limited nanopillar tip deflections, the NV$^-$ centre’s powerful magnetometry abilities can be used to measure spatial deflection of the nanopillar tip. If an NV centre was at the tip of the nanopillar and a magnetic field gradient ($\vec{\nabla} B_z$) was applied then the magnetic change of the spin resonance of the displaced NV centre would be $\Delta f_{\pm}^{\text{mag}} = \pm \gamma_e \vec{\nabla} B_z \cdot \vec{r}_{\text{tip}}(\vec{F})$. In this case the force sensitivity is limited by the magnetic sensitivity of the NV centre ($\sim 1 \mu \text{T}/\sqrt{\text{Hz}}$ for nanopillars [15]) and the magnitude of the magnetic field gradient. This case enables sub-diffraction limited tip displacements to be easily detected. For both $\Delta f_{\pm}^{\text{mech}}$ and $\Delta f_{\pm}^{\text{mag}}$ the changes in the spin-resonances are linear with tip displacement ($\vec{r}$) and force (F). Using the ratio $|\Delta f_{\pm}^{\text{mech}}| / |\Delta f_{\pm}^{\text{mag}}|$ a comparison of the spin responses for each strategy can be seen in figure 5.11(b). For the dimensions considered, the magnetic sensing techniques have a larger response if the magnetic field gradient $|\vec{\nabla} B_z| \gtrsim 30 \text{mT}/\mu \text{m}$. Such high field gradients are possible using ferromagnetic tips [176] placed very close (<100 nm) to the sample. However, such tips suffer from ferromagnetic thermal noise and positioning instability at these length scales [123]. This can result in a lower sensitivity due to detuning and increase spin dephasing. Moreover, placing the tip so close to the sample reduces the available space for varying optical and force microscopy geometries.
Figure 5.11: (a) Proposed nanopillar design for force sensing, for spin-mechanical based sensing an NV\(^{-}\) centre at the base of the nanopillar will experience the strongest bending stress. For magnetic field gradient sensing an NV\(^{-}\) centre at the tip of the nanopillar will experience the greatest spin-resonance change. (b) contour plot of the magnetic field gradient \(\nabla B_z\) that is required for the spin-magnetic response \(\Delta f_{\pm}^{\text{mag}}\) of the NV centre at the nanopillar’s tip to exceed the spin-mechanical response \(\Delta f_{\pm}^{\text{mech}}\) of the NV centre at the nanopillar’s base.
5.7 Conclusion

Force sensing was demonstrated using a diamond microcantilever. The results strongly agree with the force determined using Euler-Bernoulli bending theory. This validates the spin-mechanical model and parameters from the previous chapters and the application of Euler-Bernoulli theory to the nanoscale. The demonstrated force sensitivity is a motivation for new ideas that utilise the NV$^-$ centre for mechanical sensing. These ideas are discussed in the next chapters.
CHAPTER 6

Proposal of nano spin-mechanical devices

6.1 Contributions

These ideas were developed by M.W. Doherty and M.S.J. Barson.

6.2 Introduction

The mechanical susceptibility of the NV centre’s electron spin can be exploited together with the extreme mechanical properties of diamond nanomechanical structures to realise nano-spin-mechanical sensors (NSMS). Due to the unique nature in which the NV$^-$ centre is sensitive to crystal strain and not force; the ability to image single centres; the long NV$^-$ spin coherence time and the NV$^-$ centre’s well established ODMR sensing techniques there is scope for unique and highly optimised NSMS devices.

The two devices we propose are (1) an array of nanopillars, capable of detecting and imaging forces. This device takes advantage of the separation of the NV centre from the force contact and the ability to image a high density of single NV centres. The second device (2) is a resonating mechanical beam, using time-dependent ODMR measurements, changes in the resonant vibrations of the beam can be accurately measured and exploited for metrology. Since NV$^-$ is directly sensitive to stress and multiple centres can be measured within the one beam it is possible to measure the resonant beam frequency and image its spatial mode, allowing for unique determination of spatial information and mass sensing.
6.3 Nanopillar array force measurements

There is scope to optimise the design of NV based nanomechanical sensors due to the unique way in which it is stress within the diamond is sensed, not the deflection of a mechanical element. This allows for the sensor part of a nanomechanical sensing device to be spatially separated from the sample being sensed. Many sensors can be employed simultaneously since the only required information is the fluorescence signal from the NV\(^-\) centres. These two flexibilities led to the idea of sensing forces using a nanopillar array, as this was the simplest concept that could explore these capabilities.

The nanopillar force sensor has an NV located at the base of the nanopillar, which can be prepared into an array of nanopillars and combined with wide-field imaging. These arrays can provide parallel force measurements from each nanopillar allowing for spatial mapping of forces at very high spatial density. Each nanopillar has an NV at the base which is sensitive to the bending forces within the pillar. This bending is generated from a force acting at the tip of the pillar. Knowing both the placement of the NV within the base of the pillar, and the geometry of the pillar enable the force exerted at the tip of the nanopillar to be reconstructed.

If an array of nanopillars is used, then the information from multiple pillars can be combined to generate a vector force map. Four pillars are used to generate a superpixel that can project the force onto a 2D map. Obviously, these techniques are more suited to widefield techniques and not single site microscopy as the required number of NV centres required to generate a useful sized map would make single site microscopy slow and cumbersome. Ideally these arrays would be placed underneath a cell and its movement recorded, the traction forces exerted by cells give information about how that cell can move. This is particularly important for high mobility cells like some cancers cells and can provide information to target their treatment. Other techniques that use the deflection of nanopillar arrays have been demonstrated but the nanopillar deflections are usually measured optically and so the periodicity and deflection of the nanopillars are diffraction limited [177], for sensitive measurements the deflection of the nanopillar tip must be relatively large compared to the diffraction limit. These requirements put an upper limit on the spatial sensitivity (periodicity) and the force sensitivity of the device.

To create a spatial map of the applied force in wide-field, the nanopillars could be arranged in a array with spacing so that the diffraction limited spot of adjacent nanopillars does not overlap (spacing ≥ 250 nm). Each nanopillar at position \((i,j)\), provides a force pixel with a spin resonance change of \(\Delta f_{i,j} = (a_i \pm\)
$2b) h\bar{F}_{i,j} \cdot \bar{\xi}_{i,j}/I$ for the (+) upper and (-) lower spin branches. The dot product of $\bar{F}_{i,j} \cdot \bar{\xi}_{i,j}/I$ is the projection of the applied force $\bar{F}_{ij}$ on the NV position $\bar{\xi}_{i,j}$ within the nanopillar. If the position of the NV centre within the nanopillar is previously determined, most likely from applying a known force and measuring the spin-response, then the local force $\bar{F}_{i,j}$ can be determined. Since only the scalar projection of the local force onto the NV coordinates in that nanopillar is measured, the vector of the force is not known. However, the spin response of neighbouring nanopillars can be combined into a “super-pixel” $(I,J)$ using the neighbouring spin resonance shifts $\Delta f_{IJ}^\pm = (\Delta f_{2I-1,2J-1}^\pm, \Delta f_{2I,2J}^\pm, \Delta f_{2I-1,2J}^\pm, \Delta f_{2I,2J-1}^\pm)^T$ and a corresponding position of neighbouring NVs within their respective nanopillars $\Xi_{IJ} = (\bar{\xi}_{2I-1,2J-1}, \bar{\xi}_{2I,2J-1}, \bar{\xi}_{2I-1,2J}, \bar{\xi}_{2I,2J})^T$, as shown in figure 6.1. The in plane estimate of the super-pixel force is then $\bar{F}_{IJ} = \frac{Ih}{4\pi^2b} (\Xi_{IJ}^T \Xi_{IJ})^{-1} \Xi_{IJ}^T \bar{\Delta} f_{IJ}$. It would be practical to choose only one of the spin-resonance branches (+ or -) either by taking advantage of some inherent stress or an applied magnetic field to identify the spin-resonances. The intrinsic stress in nanostructures is often non-zero [178]. Applying a small bias field to separate the strain split branches does not effect the spin-mechanical response as shown in figure 4.5(a). Assuming that the magnetic field is kept constant throughout the experiment, its effect to the shift of the spin-resonance can simply be subtracted. Alternatively, both resonances can be recorded and their spin response can be post processed by comparing to neighbouring nanopillars. To determine the vector of the total super-pixel force $\bar{F}_{IJ}$ across the super-pixel some extra information is required, because $\bar{F}_{IJ}$ is really just a collection of scalar values that represent the projection of a local force onto a known NV location. If it is assumed that the magnitude of the force is constant across the super-pixel than the vector force can be extracted. Alternatively, if the local force direction is expected to be constant across the super-pixel then the magnitude of each component can be extracted. Even with the restriction of these approximations the high density of information from such an array would still provide an insightful force map. Uniquely, the AC dependence of the spin-mechanical interaction due to an applied time-varying force can be extracted from this array using pulsed ODMR techniques (spin-echo, CPMG, XY-8, etc.) and wide-field microscopy. The pulsed sequence can be used as a filter function to sample only signals of certain frequency bands [108]. This filtering effect could be useful to see wide-field frequency shifts of the nanopillars due to some external perturbation from the sample, for example a change in damping coefficient. The frequency of the thermal vibration of the nanopillar is far from the sensing band of the NV-centre. The first order vibration
of a free cantilever in one-dimension is given as 
\[ f_1 = \frac{3.516}{L^2} \sqrt{\frac{EI}{\rho A}} \frac{1}{2\pi} \sim 1\,\text{GHz}, \]
for the dimensions of this example nanopillar 1 GHz \( \gg 1/(T_{AC}^{min}) \sim 100\,\text{MHz} \) the maximum frequency the NV spin can practically measure. Any AC sensing with these pillars will be far from the resonant case, unlike the situations discussed in sections 6.4 and 6.5.

This array can be manufactured with existing diamond etching techniques using a top down approach of e-beam lithography (EBL) followed by reactive ion-etching (RIE) \cite{15, 172} and high precision nitrogen implantation \cite{179, 180, 181, 182, 183}. Ion implantation can have poor \( z \) accuracy due to large stopping distance straggle but quite good lateral \((x, y)\) accuracy. Conversely, delta-doping techniques \cite{179, 184} have very good \( z \) accuracy but little control over the lateral position of the nitrogen placement. Either method could be used and both have trade-offs. Initially a delta-doped layer grown in at a depth equal to the nanopillar height followed by EBL and RIE nanopillar creation would be the simplest manufacturing avenue to pursue. The delta-doped density can be tuned to provide an average of one NV per nanopillar in a random position \cite{15}. The non-optimal placement of the NV centres within the
base of the nanopillar means that only a portion of the nanopillars will be optimally useful with well placed NVs. This will give a poorer force sensitivity for small forces and imaging.

6.4 AC spin-mechanical force sensing

There are three interesting regimes of force sensing with NV\(^-\) centres in diamond:

1. DC forces - The sensing of DC forces using the NV\(^-\) spin is achieved by simply measuring the DC shift to the spin resonances due to the spin-mechanical interaction either by CW ODMR or a Ramsey measurement.

2. Resonant AC forces - AC force sensing requires the measurement of the time dependent change of the spin-resonances due to a time varying force. However, the mechanical dynamics of the system and the spin dynamics both need to be considered. Mechanical oscillators show interesting behaviour near resonance, where a large increase in amplitude and a large change in the phase of the motion occurs.

3. Non-resonant AC forces - For driving frequencies far from the resonance, the motion of the oscillator directly the driving force with minimal change in phase. The resulting interaction can be considered the same as any harmonic interaction, for example AC magnetometry.

For either AC case, the effect of the oscillator motion of the NV\(^-\) will be measured using pulsed spin-echo ODMR measurements, similar to well established AC magnetometry techniques [53, 54, 123]. As with magnetometry [185, 186], the timing of the pulses can be controlled to be selective of components of motion which are in and out of phase with the driving force. The motion of the mechanical oscillator being sensed by the NV\(^-\) is driven by a well controlled signal generator. As such, recent techniques demonstrated in NV\(^-\) AC magnetometry that perform correlation spectroscopy [115, 116] using a classical clock would be very well suited to these measurements. These techniques offer a considerable increase in acquisition speed and sensitivity for detecting classical AC signals, such as those expected for these systems.

In the case of a harmonic driving force acting on a damped harmonic oscillator, the phase and amplitude of the mechanical response are well known. The equation
of motion

\[ \ddot{\chi}_n(t) + 2\zeta_n\omega_n\dot{\chi}_n(t) + \omega_n^2\chi_n(t) = \frac{F}{m}\cos(\omega t) \quad (6.1) \]

for an under-damped \( \zeta_n < 1 \) (high \( Q_n = 1/2\zeta_n \)) system in the steady-state after the initial transient response is easily solved. The damping \( \zeta_n \) is chosen to be mode dependent, signified by the \( n \) subscript. Using a trial solution of the form

\[ \chi_n(t) = J_n\cos(\omega t) + K_n\sin(\omega t) \quad (6.2) \]

which is an expression of an in phase cosine \( (J_n) \) and out of phase sine \( (K_n) \) terms. Plugging this solution into the differential equation (6.1) and equating the sine and cosine times gives the solution

\[ J_n = \frac{F}{m} \frac{\omega^2 - \omega_n^2}{(\omega^2 - \omega_n^2)^2 + (2\omega\omega_n\zeta_n)^2} \quad (6.3) \]

\[ K_n = \frac{F}{m} \frac{2\omega\omega_n\zeta_n}{(\omega^2 - \omega_n^2)^2 + (2\omega\omega_n\zeta_n)^2}. \]

For frequencies close to resonance \( |\omega - \omega_n| \ll \omega_n \), the approximation \( \omega^2 - \omega_n^2 \approx 2\omega_n(\omega - \omega_n) \) allows the \( J_n \) and \( K_n \) components to be simplified to

\[ J_n = \frac{F}{2m\omega} \frac{\omega - \omega_n}{(\omega - \omega_n)^2 + (\omega_n\zeta_n)^2} \quad (6.4) \]

\[ K_n = \frac{F}{2m\omega} \frac{\omega_n\zeta_n}{(\omega - \omega_n)^2 + (\omega_n\zeta_n)^2}. \]

Since this solution is the harmonic addition of sine and cosine terms it can also be expressed as a single sine expression with a phase shift

\[ \chi_n(t) = Z_n\sin(\omega t + \varphi_n) \]

\[ Z_n = \sqrt{J_n^2 + K_n^2} \]

\[ \varphi_n = \arctan\left(\frac{K_n}{J_n}\right). \quad (6.5) \]

These components are shown in figure 6.2.

Combining the in and out of phase amplitudes (temporal) \( J_n \) and \( K_n \) with the spatial mode shape functions \( X_n(x) \) (equation (6.23)) gives the in phase and out of
Figure 6.2: The amplitude ($Z$) and the phase ($\varphi$) of a damped mechanical oscillator near resonance $\omega_0$ for $Q$ values $Q/2$, $Q$, $2Q$. Amplitudes are much greater near resonance with a decreasing width and increasing magnitude for increasing $Q$. The phase is defined as the lag of the motion of the oscillator behind the driver. For driving frequencies slower than resonance the phase lag is 0, at resonance it is $\pi/2$ and for frequencies faster than resonance it is $\pi$. 
phase vibration of the mechanical oscillator

\[ \psi(x, t) = \sum_{n=1}^{\infty} \psi_n(x, t) \]

\[ \psi_n(x, t) = X_n(x) \chi_n(t) \]

\[ \psi_{Jn}(x, t) = X_n(x) J_n \sin(\omega t) \]

\[ \psi_{Kn}(x, t) = X_n(x) K_n \cos(\omega t). \]

The bending stress generated from a bending moment is given by \( \sigma_{xx} = M \xi_z / I \) [169]. For an NV centre at position \( \vec{\xi} \) the bending moment and bending stress due to the \( n^{th} \) vibrational mode at \( x = \xi_x \) is,

\[ M_n(\vec{\xi}, t) = EI \left. \frac{\partial^2 \psi_n(x, t)}{\partial x^2} \right|_{x=\xi_x} \] (6.7)

\[ \sigma_{n,xx}(\vec{\xi}, t) = \frac{\xi_z}{I} M_n(\vec{\xi}, t). \] (6.8)

The shear stress due to pure bending is \( \sigma_{xy} = \frac{VQ}{Iw} \), where \( V, Q, I, w \) are the shear, the first moment of area (or statical moment), the second moment of area and the beam width, respectively. The shear is the derivative of the moment

\[ V_n(\vec{\xi}, t) = \frac{\partial}{\partial x} M_n(\vec{\xi}, t) \] (6.9)

\[ = EI \left. \frac{\partial^3 \psi_n(x, t)}{\partial x^3} \right|_{x=\xi_x}. \] (6.10)

Equations 6.8 and 6.10 show that the maximum bending and shear stress will be located at a position \( x \) along the beam where there is a vibration anti-node and node, respectively, as shown in figure 6.3(a). For a solid rectangular cross section (of height \( h \)) the shear force at a distance \( \xi_z \) from the neutral axis is [169]

\[ \sigma_{n,xz}(\vec{\xi}, t) = \frac{V_n(\vec{\xi}, t)}{2I} \left( \left( \frac{h}{2} \right)^2 - \xi_z^2 \right) \] (6.11)

which is a maximum at the neutral axis of the beam and zero at the surface of the beam. For comparison the bending stress is a maximum at the surface of the beam and zero at the neutral axis, as shown in figure 6.4(a).

Now that the mechanical solution for the harmonic oscillator is completely understood, the spin-mechanical behaviour of the NV can be investigated. For a beam with a \( \{100\} \) surface and the beam edge cut along another \( \{100\} \) direction, the stress


Figure 6.3: (a) Vibration mode \(X\) and associated moment \(M\) and shear \(V\) for the first four modes of a double clamped beam. The \(\beta\) parameters signify the different spatial modes of vibration permissible for a double clamped beam.

tensor will be \(\tilde{\sigma} = \{\sigma_{n,xx}(\vec{\xi},t), 0, 0, 0, \sigma_{n,xz}(\vec{\xi},t), 0\}\). For an NV centre very close to the surface there will be only the bending stress \(\sigma_{n,xx}(\vec{\xi},t)\), resulting in the spin resonances \(f_\pm = f + \Delta f_\pm = D + M_z \pm \sqrt{M_x^2 + M_y^2} = D + (a_1 \pm 2b)\sigma_{n,XX}(\vec{\xi},t)\), where \((x,y,z)\) and \((X,Y,Z)\) represent the NV and crystal coordinate systems, respectively. At the centre of the beam \(\xi_z = 0\), only the shear component \(\sigma_{n,XZ}(\vec{\xi},t)\) will be non-zero. Using equation (3.7) the resulting spin-resonances will be \(f_\pm = f + \Delta f_\pm = D + M_z \pm \sqrt{M_x^2 + M_y^2} = D + (2a_2 \pm 2c)\sigma_{n,XZ}(\vec{\xi},t)\).

When looking at either the bending or shear stress (or both), the spin-mechanical interaction can be generalised to a time dependent perturbation on the spin of the form \(q(t) = a \sin(\omega t + \alpha)\), where \(\alpha\) is the initial phase delay between the spin control and the interaction and \(a\) is the amplitude of the interaction. For example, if the interaction is due to bending stress

\[
q(t) = E\xi_z \frac{\partial^2 \psi_n(x,t)}{\partial x^2} \bigg|_{x=\xi_x} \\
= E\xi_z \frac{\partial^2 X_n}{\partial x^2} \bigg|_{x=\xi_x} \chi_n(t) \\
\Rightarrow a = E\xi_z \frac{\partial^2 X_n}{\partial x^2} \bigg|_{x=\xi_x} \frac{F}{m\omega \sqrt{\omega^2 - \omega_n^2} - (2\omega\omega_n\zeta_n)^2}.
\]

This interaction will result in the spin resonance frequencies \(\omega_\pm = D + (\lambda_\parallel \pm \lambda_\perp)q(t)\), where \(\lambda_\parallel\) and \(\lambda_\perp\) and the susceptibilities which describe the shift and the

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6.4. AC SPIN-MECHANICAL FORCE SENSING

Figure 6.4: (a) An element of a beam under bending deformation. The infinitesimal element \((dX, dY)\) at position \(\xi\) shows the directions of bending stress \(\sigma_{XX}\) and shear stress \(\sigma_{ZX}\). The red carbon atoms show that this beam’s longitudinal axis \(X\) is aligned in a \(\langle 100 \rangle\) direction, the possible NV orientations are all at 54° to the \(X\) axis. The bending stress \((\sigma_{XX})\) and shear stress \((\sigma_{ZX})\) profiles are shown in the bottom left, the central values are at the neutral axis where \(\xi_Z = 0\).

Figure 6.5: (a) Spin-echo pulse sequence for AC force sensing with relevant phase delays labelled. \(\beta\) is the mechanical phase lag of a Harmonic oscillator, \(\gamma\) is the controllable delay between the driven displacement and the microwave pulse signals and \(\alpha\) is the delay between the motion and the microwave pulses. \(\alpha\) is the relevant quantity to probe the motion using spin-echo measurements but the \(\gamma\) is the easily controlled quantity.
splitting of the spin resonances, respectively. For simplicity, assume that an applied magnetic field or intrinsic strain separates the ±1 spin levels and only the transition between the ground and the upper (+) or lower (−) excited spin branches is considered. The frequency change of one spin resonance, say the upper branch (+), is now \( \omega_+ = D + \lambda q(t) \), where \( \lambda \) will be a combination of parameters dependent on the applied magnetic field and strain combination. The spin-echo signal from such an oscillating interaction will be of the form \( S(\tau) = C_1 + C_2 e^{-\tau/T_2} \cos \Phi \) [54], where \( C_1 \) and \( C_2 \) are experimental parameters relating to photon count rates and spin contrast. The spin-echo envelope \( e^{-\tau/T_2} \) includes the spin de-phasing which introduces a loss of spin-echo signal with time constant \( T_2 \). The accumulated quantum phase of the NV− spin \( \Phi \) is due to the spin-mechanical interaction we wish to measure. For a spin-echo sequence the accumulated phase \( \Phi \) is

\[
\Phi = \int_{0}^{\tau/2} \lambda q(t) dt - \int_{\tau/2}^{\tau} \lambda q(t) dt \\
= \int_{0}^{\tau/2} \lambda \sin(\omega t + \alpha) dt - \int_{\tau/2}^{\tau} \lambda a \sin(\omega t + \alpha) dt \\
= -\frac{4a\lambda}{\omega} \cos \left( \frac{\omega \tau}{2} + \alpha \right) \sin \left( \frac{\omega \tau}{4} \right) \\
= -\frac{4a\lambda}{2\pi \nu} \cos \left( \pi \nu \tau + \alpha \right) \sin \left( \frac{\pi \nu \tau}{2} \right)
\]

Matching the pulse spacing to the driven frequency \( \tau = 2\pi/\omega \) the accumulated phase becomes,

\[
\Phi = \frac{4a\lambda}{\omega} \cos \alpha 
\]

For the non-resonant case, the complications of the mechanical behaviour near resonance can be ignored and all that matters is that the interaction behaves like a simple sinusoidal detuning. The interaction can be probed in the exact same fashion as AC magnetometry as the mechanical phase is not strongly dependent on frequency and will either be 0 or \( \pi \) (figure 6.2) far from resonance.

However, near resonance it is generally not possible to precisely know the relative delay between the pulse sequence and the oscillator motion (\( \alpha \)) as there is another mechanical delay between the driving force and the resulting motion (\( \beta \)). For harmonic motion at exact resonance, this delay (\( \beta \)) is a \( \pi/2 \) phase lag of the oscillator motion behind the driving force. However, the resonance is sharp for high Q resonators and this condition will be hard to exactly achieve experimentally. In contrast, the delay between the driving signal and the pulse sequence (\( \gamma \)) can easily
be controlled. For a mechanical driver-motion phase \( \beta \) the motion-pulse phase \( \alpha \) can be controlled by choosing the driver-pulse phase \( \gamma \) as shown in figure 6.5(a). By sweeping \( \gamma \) the quantum phase (\( \Phi \)) for a driven frequency (\( \nu \)) and amplitude (\( a \)) is

\[
\Phi = \frac{4a}{\nu} \lambda \cos(\gamma - \beta)
\]

\[
= \frac{4a}{\nu} \lambda (\cos \gamma \cos \beta + \sin \gamma \sin \beta)
\]  

(6.15)

(6.16)

By choosing \( \gamma \), the in (\( J \)) and out (\( K \)) of phase (\( \beta \)) components of the vibration contributions to \( \Phi \) can be selected

\[
\Phi(\gamma = 0) = \frac{4a}{\nu} \lambda (\cos \beta) = \frac{4}{\nu} \lambda K
\]

\[
\Phi(\gamma = \frac{\pi}{2}) = \frac{4a}{\nu} \lambda (\sin \beta) = \frac{4}{\nu} \lambda J.
\]  

(6.17)

(6.18)

Even though the delay between the driving force and pulse sequence (\( \gamma \)) can be freely chosen, it may not possible to set it exactly to 0, \( \pi/2 \), etc due to a combination of small undetermined delays in the cable lengths, switches or similar experimental unknowns. However, if two orthogonal values of \( \gamma \) are used \( \gamma_1 = \gamma \), \( \gamma_2 = \gamma + \frac{\pi}{2} \) then the defining parameters of the mechanical interaction can still be extracted

\[
\Phi_1(\gamma - \beta) = \frac{4}{\omega} \lambda A \sin \alpha
\]

\[
\Phi_2(\gamma - \beta + \pi/2) = \frac{4}{\omega} \lambda A \cos \alpha
\]

\[
\alpha = \arctan\left(\frac{\Phi_1}{\Phi_2}\right)
\]

\[
Z = \frac{\omega_n}{4\lambda} \sqrt{\Phi_1^2 + \Phi_2^2}.
\]  

(6.19)

### 6.5 Nanobeam mass sensing and inertial imaging

The other proposed device is a resonantly vibrating double clamped beam of diamond as shown in figure 6.6. The spin resonances of NV centres within the beam are shifted by the bending stress generated from vibrations at the frequency of the oscillations of the beam. We can probe the temporal dynamics of the system by using pulsed ODMR techniques. These temporal measurements allow sensing of changes in the beam’s resonant frequency. This change in resonant frequency can be due to the beam’s mass changing. This change in mass may be caused by an adsorbate molecule binding to the nanobeam, making this device a mass sensor. Since the
Proposed nanobeam design for mass sensing and inertial imaging. Bending moments developed within the beam will have a maximum at the turning points of the deflected beam shape. The greatest bending stress will be at the surface of the beam at this position.

NV centre is uniquely sensitive to stress (not just frequency) and can be distributed spatially within the beam, it is possible to measure the spatial amplitude distribution or shape of vibrations of the beam. This shape can tell us about the mass distribution of adsorbate on the beam. From this we can infer the distribution of mass of the adsorbent molecule, gaining information not only of its mass but also its structure. The sensing of the mass of molecules using vibrating beams has already been realised with NEMS structures [187, 188, 189, 190], but they cannot image the spatial mode like an NV$^-$ NSMS diamond beam. Resonating mechanical mass sensors provide the additional benefit that they are not sensitive to charge, this is increasingly important for large molecules where the ionisation characteristics can lead to a complicated variety of mass-charge ratio possibilities [188], complicating the results of conventional mass spectroscopy.

To describe this system we need to consider the Euler-Lagrange equation for a homogeneous beam with a regular cross section undergoing transverse vibration [191]

$$EI \frac{\partial^4 \psi(x, t)}{\partial x^4} = -\mu \frac{\partial^2 \psi(x, t)}{\partial t^2} + q(x, t),$$  \hspace{1cm} (6.20)

where $E, I, \mu = M/L, q$ are the Young’s Modulus, second moment of area, linear mass density and applied transverse load, respectively. For free vibration when $q = 0$ the solution can be obtained by the separation of variables $\psi = X(x)T(t)$,

$$\frac{EI}{\mu} \frac{d^4 X}{d x^4} = -\frac{d^2 T}{d t^2} \frac{1}{T} = \omega^2.$$  \hspace{1cm} (6.21)
The time dependent part yields the normal harmonic solution,

\[ T(t) = A \cos(\omega t) + B \sin(\omega t), \]  

(6.22)

where \( A \) and \( B \) describe the displacement and velocity initial conditions, respectively. Damping was ignored in this case, but the equation can be simply modified to the solution of the common damped harmonic oscillator. The spatial dependent part has the differential equation where \( \beta^4 = \frac{\omega^2 \mu}{EI} \),

\[ \frac{d^4X(x)}{dx^4} - \beta^4 X(x) = 0 \]  

(6.23)

which has the solution (characteristic \( \lambda^4 + \beta^4 = 0 \) equation roots are \( \pm \beta, \pm i\beta \)),

\[
X(x) = C_1 \cos(\beta x) + C_2 \sin(\beta x) + C_3 \cosh(\beta x) + C_4 \sinh(\beta x) \\
X'(x) = -C_1 \beta \sin(\beta x) + C_2 \beta \cos(\beta x) + C_3 \beta \sinh(\beta x) + C_4 \beta \cosh(\beta x). 
\]  

(6.24)

The coefficients \( C_1, C_2, C_3, C_4 \) are determined from the boundary conditions, for the case of a perfectly double clamped beam \( X(0) = X'(0) = X(L) = X'(L) = 0 \). This gives

\[
X(0) = C_1 + 0 + C_3 + 0 = 0 \\
X'(0) = 0 + C_2 \beta + 0 + C_4 \beta = 0 \\
X(L) = C_1 \cos(\beta L) + C_2 \sin(\beta L) + C_3 \cosh(\beta L) + C_4 \sinh(\beta L) = 0 \\
X'(L) = -C_1 \beta \sin(\beta L) + C_2 \beta \cos(\beta L) + C_3 \beta \sinh(\beta L) + C_4 \beta \cosh(\beta L) = 0, 
\]  

(6.25)

which can be simultaneously solved and has non-trivial solutions for \( \cos(\beta L) \cosh(\beta L) = 1 \), which can be solved numerically and has roots

\[
\beta_n = \beta_1, \beta_2, \beta_3, \ldots \\
= 1.506\pi/L, 2.500\pi/L, 3.500\pi/L, \ldots 
\]  

(6.26)

For this continuous system the time-dependent equation can have infinite resonant frequencies (\( \omega \)). However, since the spatial mode solution’s boundary conditions impose finite spatial frequencies which are linked to the temporal frequencies, there are discrete natural vibrational frequencies \( \omega_n = \beta_n^2 \sqrt{\frac{EI}{\mu}} \).
Figure 6.7: First four mode shapes for a double clamped beam from equation (6.28). The $\beta$ parameters signify the different spatial modes of vibration permissible for a double clamped beam.

Solving for the coefficients gives

$$
C_1 = -C_3 \\
C_2 = -C_4 \\
C_1 = -C_2 \frac{\sin(\beta L) - \sinh(\beta L)}{\cos(\beta L) - \cosh(\beta L)}.
$$

(6.27)

The solution for the spatial mode for a given $n$ have the form,

$$
X_n(x) = C_n \left( \cos(\beta_n x) - \cosh(\beta_n x) - \frac{\cos(\beta_n L) - \cosh(\beta_n L)}{\sin(\beta_n L) - \sinh(\beta_n L)} \left( \sin(\beta_n x) - \sinh(\beta_n x) \right) \right),
$$

(6.28)

the first four spatial modes are shown in figure 6.7. These modes satisfy the orthonormality relation

$$
\int_0^L X_n(x)X_m(x)dx = \delta_{n,m} L.
$$

(6.29)

Equation 6.23 is an eigenvalue problem with eigenfunctions $X_n$ and eigenvalues $\beta_n^4$. Using these normalised spatial modes, a general solution to the deflection profile can be described as

$$
X(x) = \sum_{n=1}^{\infty} C_n X_n(x).
$$

(6.30)
6.5. NANOBEAM MASS SENSING AND INERTIAL IMAGING

Drawing on methods outlined for mass spectroscopy with NEMS resonating mechanical beams [187, 188, 192], in which a mass attaches rigdly to the beam and its size is small compared to the spatial wavelength of the vibration. Perturbation theory can be applied to determine the modified frequency and modes of the vibration due to a small change in the linear density of the beam \( \mu_0 \rightarrow \mu_0 + \mu_1(x) \), for \( \mu_1(x) \ll \mu_0 \). Since this is a regular non-degenerate time-independent eigenvalue problem (time-independent for steady state harmonic motion), the same well known perturbation methods used in quantum mechanics can be applied [193]. Using the Taylor expansion

\[
\frac{1}{\mu_0} \rightarrow \frac{1}{\mu_0 + \mu_1(x)} \approx \frac{1}{\mu_0} - \frac{\mu_1(x)}{\mu_0^2} + \ldots
\]

(6.31)

The modification to the spatial differential equation

\[
\frac{EI}{\mu_0} \frac{d^4X_n(x)}{dx^4} = \omega_n^2 X_n(x)
\]

(6.32)

is the addition of

\[
-\frac{\mu_1(x)}{\mu_0^2} EI \frac{d^4}{dx^4}.
\]

(6.33)

Comparing to quantum mechanics, this is the same as \( E_n^{(1)} = \langle n^{(0)} | V | n^{(0)} \rangle \) for the system \( H|n\rangle = E_n|n\rangle \rightarrow (H_0 + V)|n\rangle = E_n|n\rangle \). The perturbed eigenvalues are \( (\omega_n^2)^{(1)} = (\omega_n^2)^{(0)} + \Delta(\omega_n^2) \). Where the correction \( \Delta(\omega_n^2) \) is,

\[
\Delta(\omega_n^2) = -\frac{1}{l} \int_0^l X_n(x) \frac{\mu_1(x)}{\mu_0^2} EI \frac{d^4}{dx^4} X_n(x)dx
\]

(6.34)
Expanding and equating $(\omega + \Delta \omega)^2$ to linear terms $a$ and $\Delta a$,

$$(\omega + \Delta \omega)^2 = a + \Delta a$$

$$\omega^2 + 2\omega \Delta \omega + (\Delta \omega)^2 = a + \Delta a$$

Let $\omega^2 = a$

$$\Rightarrow 2\omega \Delta \omega + (\Delta \omega)^2 = \Delta a$$

$$2 \frac{\Delta \omega}{\omega} + \left(\frac{\Delta \omega}{\omega}\right)^2 = \frac{\Delta a}{\omega^2}$$

Since $\left(\frac{\Delta \omega}{\omega}\right)^2 \approx 0$

$$\Delta \omega = \frac{\Delta a}{2\omega}$$

Using the above expansion the frequency shift in equation (6.34) can be written as

$$\Delta \omega_n = -\frac{\omega_n}{2l} \int_0^l \frac{\mu_1(x)}{\mu_0} X_n(x)^2 dx.$$  \hspace{1cm} (6.36)

The change to the modes can also be determined by simply substituting into the well known quantum mechanics analogue

$$|n^{(1)}\rangle = \sum_{n \neq m} \frac{\langle m^{(1)}|V|n^{(1)}\rangle}{E_n^{(0)} - E_m^{(0)}} |m^{(0)}\rangle,$$  \hspace{1cm} (6.37)

the perturbed eigenfunction become $X^{(1)}_n(x) = X_n(x) + \sum_{n \neq m} c_{nm} X_m(x)$, where the mode coupling constants $c_{nm}$ are,

$$c_{nm} = \frac{1}{w_n^2 - w_m^2} \frac{1}{l} \int_0^l X_m(x) - \frac{E_I}{\mu_0} \frac{d^4}{dx^4} X_n(x) dx$$

$$= -\frac{w_n^2}{w_n^2 - w_m^2} \frac{1}{l} \int_0^l \frac{\mu_1(x)}{\mu_0} X_m(x) X_n(x) dx.$$  \hspace{1cm} (6.38)

Now the damped harmonic oscillator equation (6.1) is solved but modified for the perturbed resonant frequency $\omega_n \rightarrow \omega_n + \Delta \omega_n$. It is also assumed that the damping ($\zeta_n$ or $Q_n = 1/2\zeta_n$) is not changed by the small frequency shift,

$$\ddot{x}_n(t) + \Gamma_n \dot{x}_n(t) + (\omega_n + \Delta \omega_n)^2 x_n(t) = \frac{F}{m_0} \cos(\omega t).$$  \hspace{1cm} (6.39)
which has the usual solution

\[ \chi_n(t) = J_n \cos(\omega t) + K_n \sin(\omega t) \]

\[ J_n = \frac{F((\omega_n + \Delta\omega_n)^2 - \omega^2) / m_0}{((\omega_n + \Delta\omega_n)^2 - \omega^2) + (\Gamma_n \omega)^2} \]  \hspace{1cm} (6.40)

\[ K_n = \frac{F \Gamma_n \omega / m_0}{((\omega_n + \Delta\omega_n)^2 - \omega^2) + (\Gamma_n \omega)^2}. \]

Substituting \( \Gamma_n = Q / \omega_n \) and for resonant excitation \( \omega - \omega_n = \Delta\omega_n \) with \( \Delta\omega_n \ll \omega_n \), expanding to first order in \( \Delta\omega_n \) the solution simplifies to

\[ J_n = 2 \frac{F \Delta\omega_n}{m_0 \Gamma_n^2 \omega_n} = 2 \frac{Q_n^2 F \Delta\omega_n}{m_0 \omega_n^2} \]  \hspace{1cm} (6.41)

\[ K_n = \frac{F}{m_0 \Gamma_n \omega_n} = \frac{F Q_n}{m_0 \omega_n^2}. \]

The mass perturbation increases the in phase component of the motion, in agreement with increasing detuning for the un-perturbed case, as shown in figure 6.2. The contribution of the perturbative mass changes to the spin-resonance (\( \Delta f_\pm \)) is due to both a change in the resonant frequency and a change in the vibrational mode. Using equation (6.8) to determine the frequency shift due to bending stress and assuming the bending stress is for a cantilever aligned along a \( \langle 100 \rangle \) direction for a near surface NV, the spin-stress susceptibility is \((a_1 \pm 2b) \) (MHz/GPa) giving

\[ \Delta f_\pm = 2 \frac{Q_n \Delta\omega_n}{\omega_n} \beta_n^\pm(\xi) \sin(\omega_n t) + \sum_{n \neq m} c_{nm} \beta_m^\pm(\xi) \cos(\omega_n t), \]  \hspace{1cm} (6.42)

where \( \beta_n^\pm(\xi) \) is a collection of parameters not dependent on time

\[ \beta_n^\pm(\xi) = \frac{F Q_n}{m_0 \omega_n^2} (a_1 \pm 2b) \xi E \left| \frac{d^2 X_n}{dx^2} \right|_{\xi_n}. \]  \hspace{1cm} (6.43)

By using a spin-echo sequence that is frequency matched (same period) to \( \omega_n \) but out of phase with the resonant motion, the relative change in the accumulated spin-echo quantum phase due to the perturbative mass is

\[ \Delta \phi_{\text{out}}^\pm = 2 \frac{Q_n \Delta\omega_n}{\omega_n} \beta_n^\pm(\xi). \]  \hspace{1cm} (6.44)

Similarly, the vibrational in phase contribution to the change in the spin-echo accumulated quantum phase is from the coupling of extra modes due to the perturbative
mass

\[ \Delta \Phi_n^{in} = \sum_{n \neq m} c_{nm} \beta_m^\pm(\xi). \]  

(6.45)

To determine the adsorbate mass from the frequency shift, Hanay et al [192] defined a method that estimates the moment of mass \((m^{(k)})\) of the adsorbate based on the vibrational modes

\[
m^{(k)} = \int_0^l \mu_1(x) x^k dx
\]

\[
= \int_0^l \mu_1(x) \sum_n \alpha_{kn} X^2_n(x) dx
\]

\[
\approx m_0 \sum_n \alpha_{kn} \frac{\Delta \omega_n}{\omega_n}
\]

\[ x^k = \sum_n \alpha_{kn} X^2_n(x). \]  

(6.47)

The coefficients \(\alpha_{kn}\) are found by least-squares estimation and listed in appendix B.1. This method is problematical because measuring higher order moments requires more modes to be measured. However, the displacement (and stress) of higher order modes is increasingly small as \(Q\) typically reduces with increasing mode frequency. Nonetheless, this method is useful for determining the zeroth moment, the mass of the adsorbate \(m^{(0)} = m_0 \frac{\Delta \omega_n}{\omega_n}\). Using the generic relations (equation (2.7)) outlined in section 2.1.3, the sensitivity in detecting the change in the frequency from the spin-echo signal is,

\[
\eta_{\Delta \omega_n/\omega_n} = \left(2\pi K \frac{d\Delta \Phi_n^{+,out}}{d\Delta \omega_n/\omega_n} \sqrt{1/\omega_n}\right)^{-1}
\]

(6.48)

\[
= \left(4\pi K Q_n \beta^+_n(\xi) \sqrt{1/\omega_n}\right)^{-1}
\]

(6.49)

\[ m_{\min} = m_0 \eta_{\Delta \omega_n/\omega_n}. \]  

(6.50)

To estimate the mass sensitivity, only the first beam resonance \(\omega_1 = \beta^2_1 \sqrt{\frac{EL}{m_0}}\) with the mode shape specified in equation (6.28) is considered. For a beam of dimensions \(w \times h \times L = 0.1 \times 0.1 \times 5 \mu m^3\) and diamond density \(\rho = 3512 kg/m^3\) the beam mass is \(m_0 = 1.75 \times 10^{-16}\) kg and the first resonant frequency is \(\omega_1 = 4.7 \times 10^8\) rad/s = 75 MHz. The driving force is fixed to result in a maximum transverse displacement of \(L/10,\)
6.5. NANOBEAM MASS SENSING AND INERTIAL IMAGING

Figure 6.8: Comparison of alternative MEMS and NSMS mass sensing technologies sensitivities vs sensor volume [192].

this to remain in the small displacement limit required for Euler-Bernoulli theory. Using a typical in air $Q_n \approx 100$ [33], a maximum displacement of $L/10$ requires a force amplitude $F = 1.2 \times 10^{-7}$ N and results in a maximum bending stress of $\approx 20$ GPa at the the position $(\xi_x, \xi_z) = (L/2, h/2)$, this stress is well within the tensile strength limit of diamond ($\geq 100$ GPa [194]). For a NV− at the position of maximum bending stress and assuming that the beam is aligned along a $\langle 100 \rangle$ direction with a stress susceptibility of $(a_1 + 2b)$ MHz/GPa for the $m_s = +1$ spin branch. The resultant sensitivity in $\Delta \omega_n$ due to the adsorbate is $\eta_{\Delta \omega_n}^\pm = 0.000065/\sqrt{\text{Hz}}$ giving a minimum detectable mass of $\approx 1$ zg within $\sim 1$ s of integration time. The higher order vibration modes have the same fundamental sensing relationship, but very large forces are required to meet a comparable displacement condition of $L/10$. For the same driving force as required for $L/10$ maximum displacement of the first resonance, the higher order modes show a reduced force sensing capability. The comparable mass sensitivities for alternative technologies are shown in figure 6.8.

To gain more information of the adsorbate than just its mass, the frequency shift and the $\alpha$ parameters defined by Hanay et al [192] can be used to determine higher order moments of mass, as shown in equation (6.46). However, these methods cannot determine the actual spatial distribution of mass of the adsorbate. The NV− centre is directly sensitive to changes in stress, not just frequency. As shown in equation (6.45), by measuring the in-phase changes to the quantum phase signal $\Delta \Phi_n^{\text{in}}$, the coupling coefficients $c_{nm}$ describing the perturbation to the spatial mode can be directly measured. Using information from the coupling coefficients $c_{nm}$, the spatial distribution of mass of the adsorbate can be determined. Consider a mass located at position $x'$, the perturbation to the linear mass density can then be approximated
By a $\delta$ function,

$$\mu_1(x) = \int_0^l \mu_1(x')\delta(x-x')dx' \quad (6.51)$$

By defining coefficients $p(x')$ that describe $\delta(x-x')$ as a combination of the vibration modes $X_n(x)$

$$\delta(x-x') \approx \left[ \sum_n p_n(x')X_n(x) \right]^2, \quad (6.52)$$

the linear mass density can be re-described as

$$\mu_1(x) = \int_0^l \mu_1(x') \left[ \sum_n p_n(x')X_n(x) \right]^2 dx' \quad (6.53)$$

Expanding the sum within the square and collecting $n$ and $n \neq m$ terms,

$$\mu_1(x) = \sum_{n,m} \int_0^l \mu_1(x')p_n(x)p_m(x)X_n(x')X_m(x')dx'$$

$$= \sum_n p_n^2(x) \int_0^l \mu_1(x')X_n^2(x)dx'$$

$$+ \sum_{n \neq m} p_n(x)p_m(x) \int_0^l \mu_1(x')X_n(x')X_m(x')dx'. \quad (6.54)$$

These integrals are the perturbations of the resonant frequency $\Delta\omega_n(x)$ and the coupling coefficients $c_{nm}$, equations 6.34 and 6.38, respectively.

$$\mu_1(x) = -m_0 \left[ \sum_n p_n^2(x) \frac{\Delta\omega_n}{\omega_n} \right.$$

$$\left. + \sum_{n \neq m} p_n(x)p_m(x) \frac{w_n^2 - w_m^2}{w_n^2} c_{nm} \right]. \quad (6.55)$$

These components, can be measured independently using the in/out of phase spin-echo measurements previously defined. The linear coefficients $p_n(x)$ can be determined by multiplying equation (6.52) by $X_m(x)$, integrating and taking advantage of the orthogonality relation $\int_0^l X_n(x)X_m(x)dx = L\delta_{nm}$, giving

$$p_n(x') = \frac{1}{L} \int_0^l \sqrt{\delta(x-x')}X_n(x)dx. \quad (6.56)$$
6.6 CONCLUSION

By approximating $\delta(x - x')$ with a normalised Gaussian function for small $\sigma$

$$\delta(x - x') = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-x')^2}{2\sigma^2}}, \quad (6.57)$$

and since $X_n(x)$ is in general sinusoidal, combined with the above Gaussian expression for $\delta(x - x')$ gives the coefficients $p_n(x') \propto e^{-i\beta_n x'} e^{-\beta_n^2 \sigma^2}$. This expression for $p(x')$ is the similar to a Fourier transform with Fourier space variable $\beta_n$, where $\beta_n$ is of the form $2\pi n/L$. To determine a real space Gaussian feature of width $\sigma$ then a Fourier space Gaussian of width $\propto 1/\sigma$ must be measured. This is because the Fourier transform of a Gaussian is another Gaussian $\mathcal{F}[e^{-\pi x^2}] \propto e^{-\pi k^2 \sigma^2}$ of reciprocal width, as shown in figure 6.9. To measure a Fourier space Gaussian of width $1/\sigma$, measurements up to $1/\sigma = \beta_n \sim 2\pi N/L$ along the Fourier space axis must be performed. This means that the first $N \sim L/2\pi \sigma$ modes must be measured. As such, to increase the spatial precision of the adsorbate mass more vibrational modes must be measured.

Since many NV centres can be places within one beam, additional measurements of the coupling coefficients $c_{nm}$ can be performed by measuring multiple spatially separated NV centres in the same mode. This reduces the requirement of measuring higher and higher frequency modes to collect more information of mode coupling coefficients $c_{nm}$, which as previously discussed is increasingly difficult.

6.6 Conclusion

There is significant scope for the NV$^-$ spin-mechanical interaction to provide alternate solutions for force and mass sensing that other technology and techniques strive to achieve. Due to the remarkable room temperature properties of the NV$^-$ centre and the extreme material properties of diamond, very sensitive mechanical
measurements are possible. For example, taking advantage of the small size of NV$^-$ force sensors, high density images of forces can be measured using dense arrays of nano-mechanical sensors. Similarly, due to the unique way in which the NV$^-$ centre is directly sensitive to stress, resonant mechanical mass sensors can not only measure the mass but also image the mass distribution of molecules that adsorb onto the mass sensor. The NV$^-$ centre is advantageous in that its other sensing protocols (magnetometry, thermometry and electrometry) are gained with little or no extra device engineering challenges. Therefore, an NV$^-$ device could perform many alternate measurements on a single nanoscopic sample. A feat that would normally require multiple different dedicated metrology devices.
Part II

Temperature Interaction
CHAPTER 7

Temperature shifts of the NV$^-$ energy levels

7.1 Contributions

The theoretical details of the temperature shift in this section were developed by M.W. Doherty based on ideas from G. Davies. The experimental design, data collection and analysis were performed by M.S.J. Barson, N.B. Manson and M.W. Doherty.

7.2 Introduction

This section provides the theoretical framework and experimental evidence to explain the temperature shift of the visible and infra-red zero-phonon lines (ZPLs), and the ground state spin resonance. Results for all three resonances are experimentally collected and the extracted parameters detailed.

Although well characterised, before this work there was no satisfactory explanation of the temperature shifts of the NV$^-$ spin resonances. This explanation is important because:

- At a fundamental level, these energy shifts are due to interactions of the NV$^-$ centres with the thermal expansion of the crystal and electron-phonon processes. Understanding the thermal interaction provides fundamental knowledge of the microscopic details of the electronic orbits and spin-density of the NV$^-$ centre.
- Understanding the precise details of the temperature shift of NV$^-$ spin resonance will allow for more sensitive thermometry using the NV$^-$ spin over a larger temperature range.
- A better understanding of the optical ZPL temperature dependence will allow for greater abilities in using the NV$^-$ centre as a single photon source for
quantum information and optical coupling of separate NV− centres. As these systems often rely on stable optical lines that do not shift.

- Studying the effect of temperature can provide a greater understanding of the electron-phonon processes of the NV− centre. This will enhance understanding of their role in the optical spin-polarisation and optical spin read-out; both of which are completely critical for useful application of the NV− centre.

7.3 Theoretical framework

There are two distinct contributions to the model of the energy shifts presented here:

- A contribution from the thermal expansion of the crystal. This expansion changes the crystal environment that the defect sees altering the molecular orbitals and spin density of the NV− centre’s electrons;

- A contribution from quadratic electron-phonon interactions that create differences in the phonon distributions of the ground and excited electronic states which in turn modify the thermal average ZPL. This behaviour is quadratic in the mass-weighted nuclear displacement ($Q$).

Similar to the mechanical behaviour, the first description of the temperature behaviour of the NV− centre was of the visible ZPL by the Davies [63]. Here, that model is extended to the NV− infra-red ZPL and the ground-state spin-resonance $D$. The first contribution to the model described by Davies is a linear shift due to thermal expansion. As temperature is increased, the position of the surrounding nuclei move. The resulting shift in energy can be described as

$$
\Delta E_{ex}(T) = \frac{\partial \Delta E_{el}}{\partial Q_{ex}} \bigg|_0 Q_{ex}(T),
$$

where $\Delta E_{el}$ is the change in energy difference between two electronic levels and $Q_{ex}(T)$ is the mass-weighted nuclear displacement coordinate of thermal expansion. The above relation signifies that the energy shift due thermal expansion term is linear in terms of the coordinate shift of the nuclei $Q_{ex}$. The modes that are described by $Q_{ex}$ are the breathing modes or expansions of the entire crystal. This energy shift can be re-described equivalently by the a stress shift from the hydrostatic pressure created from thermal expansion,

$$
\Delta E_{ex}(T) = a_1 P(T),
$$
where \( a_1 \) is the hydrostatic pressure susceptibility of the resonance shift and

\[
P(T) = B \int_0^T e(T\prime) dT\prime,
\]

is the pressure arising from thermal expansion, \( B = (C_{11} + 2C_{12})/3 \) is the bulk modulus of diamond, \( C_{11} \) and \( C_{12} \) are components of the stiffness tensor and \( e(T) \) is the volumetric thermal expansion of diamond. The hydrostatic pressure shift of the optical [32, 45], infra-red [66] and spin resonance (\( D \)) [32, 195] of the NV\(^-\) centre are also well known. The thermal expansion [196, 197] and stiffness properties of diamond [165] are well known. Thus, the shift of the resonances due to thermal expansion is completely specified. The thermal expansion of diamond is often described using a power series \( e(T) = \sum_{i=1}^{4} e_i T^i \), which is integrated to another power series \( \int_0^T e(T\prime) dT\prime = \sum_{i=1}^{4} \frac{e_i}{i+1} T^{i+1} \). This allows the thermal expansion component of the shift to the electronic levels to be written as,

\[
\Delta E_{ex}(T) = a_1 P(T) = a_1 B \sum_{i=2}^{5} \frac{e_i - 1}{i} T^i.
\]  

The second component of Davies’ model is due to electron-phonon coupling which is quadratic in nuclear position \( (Q_i Q_j) \). This quadratic coupling introduces a difference in vibrational energy levels between the two electronic states. The total electron-phonon contribution to the energy shift is given by performing the thermal average over the available vibrational levels of the same vibrational number between the two electronic states (i.e. the zero-phonon transitions). As shown in figure 7.1 the differing vibrational potential and energies of the two electronic levels introduces a shift in the thermal average over all the zero-phonon electronic transitions. Using the vibrational density of modes \( \rho(\omega) \) and the thermal distribution \( n(\omega, T) = (e^{\hbar \omega/k_BT-1} - 1)^{-1} \), the thermal average is the integral over all phonon frequencies is

\[
\Delta E_{e-p}(T) = \hbar \int_0^\Omega n(\omega, T) \delta(\omega) \rho(\omega) d\omega;
\]

where \( \Omega \) is the cut-off frequency for the model (discussed later) and \( \delta(\omega) \) is the average vibrational frequency difference between the electronic states for a mode which has a frequency \( \omega \) in the initial state. The difference of the vibrational energy between the electronic states is due to the different curvature of the vibrational potential energy curves in each electronic state, as shown in figure 7.1. As such, for differences in energies much less than the vibrational frequencies \( (\delta \ll \omega) \), the
7.3. THEORETICAL FRAMEWORK

Figure 7.1: The effect of the different vibration levels distribution/curvature on the electronic transition energy. Arrows are all zero-phonon transitions, between vibrational states of the same quantum number. The total zero-phonon transition is determined from the thermal average of all zero-phonon transitions. The lower left inset plot represents that the populations of the different vibrational levels are not equal and are also dependent on temperature.

The difference in energy is given as,

\[
\delta(\omega) \rho(\omega) \approx \frac{1}{2\omega} \sum_{\alpha} \left. \frac{\partial^2 \Delta E_{el}}{\partial Q^2_{\alpha}} \right|_0 .
\]  

The sum in the above expression is over all zero-phonon transitions that start in the initial state with a frequency \( \omega \).

Since low frequency \( (\omega \to 0) \) vibrations are translations of the entire crystal, they are not expected to contribute to the change in energy levels. Therefore, the lowest power of frequency \( \omega \) which is expected to contribute to the energy differences \( \delta(\omega) \) is taken as \( \omega \). Additionally, Maradudin’s [198] and consequently Davies’ [63] assumption that the quadratic phonon coupling \( (Q_i Q_j) \) can be described by the square of linear phonon couplings is applied. Given that each linear coupling is \( \propto \sqrt{\omega} \) then their square is \( \propto (\sqrt{\omega})^2 \propto \omega \) [198]. Combining these pieces of evidence results in a quadratic electron-phonon coupling that has the lowest power of frequency \( \delta(\omega) \propto \omega \). The density of states follow the expect acoustic branch Debye distribution \( \rho(\omega) \to \omega^2 \) [198]. Therefore the product of \( \delta(\omega) \) and \( \rho(\omega) \) has the lowest power of \( \omega^3 \). As such, it is described as a power series \( \delta(\omega) \rho(\omega) = \sum_{i=3} a_i \omega^i \). Which in turn
can be evaluated as a power series commencing at $T^4$,

$$
\Delta E_{e-p} = \hbar \int_0^\Omega n(\omega, T) \delta(\omega) \rho(\omega) d\omega
= \hbar \sum_{i=3}^{\infty} \frac{a_i \omega^i}{e^{\hbar \omega / k_B T} - 1} d\omega
= \hbar \sum_{i=3}^{\infty} a_i \left( \frac{k_B T}{\hbar} \right)^{i+1} \Gamma(i+1) L(i+1, 1)
= \sum_{i=4} b_i T^i,
\tag{7.7}
$$

where $\Gamma(i)$ and $L(i, 1)$ are the gamma and polylogarithm functions, respectively, and $b_i = \hbar \left( \frac{2\pi}{\Omega} \right)^i \Gamma(i) L(i, 1) a_{i-1}$. The integral was evaluated for Debye frequency $\Omega \rightarrow \infty$ which is valid if the density of states are enforced to be 0 at $\omega > \Omega$ or the thermal population of the modes $\omega > \Omega$ is negligible, i.e. $k_B T \ll \hbar \Omega$. Normally for this type of integral over all phonon frequencies, the Debye frequency ($\Omega \sim 165 \text{ meV} [199]$) would be used as the upper limit on the integral. However, implied in our assumption of using the acoustic phonon branch and the associated density of states $\rho(\omega) \rightarrow \omega^2$, the upper frequency limit of the integral is lower than the Debye frequency. Other publications [81, 200] have put the limit on acoustic phonons in diamond at approximately $\Omega \approx 50 \leftrightarrow 80 \text{ eV}$, corresponding to an upper temperature limit of approximately $T \ll 700 \leftrightarrow 1000 \text{ K}$. As such, temperatures near and below room temperature will safely ensure that only acoustic branch phonons are populated, the requirement for the validity of this model.

Since both components $\Delta E_{ex}$ and $\Delta E_{e-p}$ are now expressed as power series in temperature, the total zero-phonon line energy shift can also be expressed as a power series polynomial

$$
\Delta E(T) = \Delta E_{e-p} + \Delta E_{ex}
= \sum_{i=4} b_i T^i + AB \sum_{i=2}^{5} \frac{e_{i-1} T^i}{i}
= -\frac{e_1}{2} AB T^2 - \frac{e_2}{3} AB T^3 - \left( b_4 + \frac{e_3}{4} AB \right) T^4 - \left( b_5 + \frac{e_4}{5} AB \right) T^5 + \ldots
\tag{7.8}
$$
Visible, infra-red ZPL and ODMR spectra were taken from dense NV$^-$ ensembles in irradiated type-1b diamond, the samples were treated with the same method described in section 4.3. For measurements above room temperature, a temperature controlled hot plate with a vacuum chuck to clamp samples onto the hot plate was used. Below room temperature a Janis liquid helium bath cryostat with a LakeShore DT670 temperature sensing diode and nichrome resistive heater mounted around the sample holder was used. A LakeShore 330 controller used PID control to maintain set point temperatures using the heater. Spectra were taken using a Jobin-Yvon spectrometer with either a photo-multiplier tube (PMT) or Ge detector for visible and infra-red emission, respectively. For the Ge detector, an optical chopper and lock-in amplifier are required as the detector has a large background. The optical transition of NV$^-$ was excited using a 100 mW 532 nm CW laser and the microwave ground state transition was excited using a two-wire transmission line with a microwave signal generator (Wavetek) and amplifier (Mini-Circuits). White light absorption spectroscopy was also performed using a tungsten light globe (Ocean Optics LS-1) and passing the transmitted light into the spectrometer. For some of the ground state $D$ measurements, unwanted magnetic fields that were present in the ferromagnetic iron hotplate needed to be eliminated. A second simple ceramic hotplate with a nichrome resistive heater using a K-type thermocouple, homebuilt amplifiers and an Arduino with PID feedback was constructed. The iron hotplate was preferred for non-ODMR (optical ZPL) measurements as it had greater thermal contact and thermal stability. The high temperature system is shown in figure 7.2.
CHAPTER 7. TEMPERATURE SHIFTS OF THE NV\textsuperscript{−} ENERGY LEVELS

Figure 7.2: Depiction of ensemble high-temperature experiment, with dashed lines representing optical spectroscopy configuration. A vacuum chuck held the sample fixed against the heater for good thermal contact. Microwaves were supplied by a two-wire transmission line. The emission was measured with either a PMT for ODMR spectroscopy or diverted into a spectrometer for the optical spectroscopy. The spectrometer had various gratings and output ports for both visible and IR detectors. If required, a lock-in amplifier could be used for ODMR by chopping the microwave signal with a switch or for spectroscopy by use of an optical chopper. The low temperature experiment is very similar except the hotplate is swapped for a Janis bath cryostat and LakeShore temperature controller.
7.5 Results and discussion

The resulting visible and infra-red ZPL spectra are shown in figures 7.4(a) and 7.4(b) respectively. The ground state ODMR spectra is shown in figure 7.3. The large signal-to-noise achieved with the lock-in amplifier shows that the P1 and $^{13}$C resonances are clearly noticeable in the ODMR spectra; features not normally obvious in ensemble ODMR spectra. The effect of temperature on the $^{13}$C ODMR hyperfine resonance is discussed in detail in chapter 8. The P1 resonances are not of interest here, they are due to interactions with nearby P1 centres (single neutrally charged substitutional nitrogen defects [201]). More information can be found in the article by Simanovskaia et al [202].
Figure 7.3: Temperature dependence of the ODMR $D$ resonance. Due to the high signal-to-noise the P1 and $^{13}$C centres can be easily seen when using a lock-in amplifier on the microwave signal.
7.5. RESULTS AND DISCUSSION

Figure 7.4: (a) The absorption spectra of the NV⁻ visible ZPL for temperatures between 5 K and 325 K. (b) The emission spectra of the NV⁻ IR ZPL for temperatures between 10 K and 500 K. The lines are Lorentzian fits to the data shown in blue. Approximate shift of the ZPL central positions is shown by the dashed line. The absolute values of the spectra are shifted for clarity. The small spikes are from γ-rays interacting with the Ge detector.
7.5.1 Comparison of data to previous descriptions

As shown in figures 7.5(a) and 7.5(b), the experimental results for the change in the zero-field splitting ($D$) agree well with the polynomial expressions already established by Chen et al [131] for low temperature and Toyli et al [31] for high temperature. The discrepancy (difference in approximate mean slope) for the high temperature data would most likely be due to a systematic error in determining the temperature. This is possibly due to the home-mode difference amplifiers (simple op-amps) of the thermocouple signal used in this particular high temperature ODMR measurement. It could also be the result of poor thermal contact, as the simple ceramic heater did not use a vacuum chuck. Even so, the high temperature descriptions are still in relatively good agreement, but it was decided to use only the low temperature data for the published parameter values [135], as we were uncertain if our calibration was wrong or the previously published expressions [31] were incorrect. The low temperatures were measured using a well calibrated LakeShore DT670 temperature sensing diode and are expected to be very reliable.
7.5. RESULTS AND DISCUSSION

Figure 7.5: (a) Low temperature $D$ shift data compared to theoretical model from Chen et al [131] and Doherty et al [135] (this work), experimental error bars are too small to be seen. (b) High temperature $D$ shift data compared to the model from Toyli et al [31] Y axis error bars were determined from Monte-Carlo analysis of the fit error (see appendix B.3). X error bars are from an estimate of instrumental read-out error.
7.5.2 Fit to the model

For all three types of spectra there is only a shift of the central position to lower energy with increasing temperature. There is no splitting to any of the lines, though there is broadening of the optical resonances. The polynomial shift of the ZPL peak energies can be seen in figure 7.6.

When fitting to the model in equation (7.8), only the electron-phonon terms \( b_4 \) and \( b_5 \) are optimised; fixed values for the expansion of diamond \( (e_i) \), bulk modulus of diamond \( (B) \) and the hydrostatic pressure shift parameter \( (a_1) \) are used. The dashed lines in figure 7.6 show the contribution from the fixed expansion only term. Due to the previously mentioned limitations on the high temperature validity of the model, and questions over the accuracy of the high temperature spin resonance data, only the below room temperature data was used to fit the parameters listed in table 7.1.

The expansion of \( \Delta E_{e-p} \) was terminated at \( T^5 \) because termination at \( T^4 \) did not yield a sufficient fit, and termination at \( T^6 \) had a negligible effect on reducing the fit error.

The significant failure of the dashed line shown in figure 7.6 to describe the observed shift demonstrates the requirement of including the quadratic electron-phonon component to explain the behaviour. This dominance of the electron-phonon interaction is beneficial for thermometry since the thermal expansion of diamond differs significantly with nitrogen impurity density. The effect of nitrogen concentration on the thermal expansion and the resonance shift is discussed in more detail in the next section.

For the case of nanodiamonds there is also a non-zero lower phonon frequency of the integral in equation (7.7) for a spherical nanoparticle, the longest possible acoustic mode wavelength is the circumference \( \lambda_{\text{max}} = 2\pi r \). Using the transverse speed of sound in diamond \( (v_t = \sqrt{C_{44}/\rho} \approx 12500\text{ m/s}, C_{44} \approx 576\text{ GPa} [203]) \) the minimum

<table>
<thead>
<tr>
<th>Shift (Unit)</th>
<th>( \Delta D ) (MHz)</th>
<th>( \Delta E_{\text{vis}} ) (meV)</th>
<th>( \Delta E_{\text{IR}} ) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_1 ) (Unit/GPa)</td>
<td>14.6</td>
<td>5.75</td>
<td>1.45</td>
</tr>
<tr>
<td>( \Delta b_{4,1} ) (Unit/( T^2 ))</td>
<td>( 39.7 \times 10^{-7} )</td>
<td>( 15.6 \times 10^{-7} )</td>
<td>( 3.95 \times 10^{-7} )</td>
</tr>
<tr>
<td>( \Delta b_{4,2} ) (Unit/( T^3 ))</td>
<td>( -91.6 \times 10^{-9} )</td>
<td>( -36.1 \times 10^{-9} )</td>
<td>( -9.12 \times 10^{-9} )</td>
</tr>
<tr>
<td>( \Delta b_{4,3} ) (Unit/( T^4 ))</td>
<td>( 70.6 \times 10^{-11} )</td>
<td>( 27.9 \times 10^{-11} )</td>
<td>( 7.03 \times 10^{-11} )</td>
</tr>
<tr>
<td>( \Delta b_{5,1} ) (Unit/( T^5 ))</td>
<td>( -60 \times 10^{-14} )</td>
<td>( -23.7 \times 10^{-14} )</td>
<td>( -5.97 \times 10^{-14} )</td>
</tr>
<tr>
<td>( b_4 ) (Unit/( T^4 ))</td>
<td>( 18.7(4) \times 10^{-10} )</td>
<td>( 8.0(8) \times 10^{-10} )</td>
<td>( 1.9(7) \times 10^{-11} )</td>
</tr>
<tr>
<td>( b_5 ) (Unit/( T^6 ))</td>
<td>( -41(2) \times 10^{-15} )</td>
<td>( -14(3) \times 10^{-13} )</td>
<td>( -3(1) \times 10^{-15} )</td>
</tr>
</tbody>
</table>

Table 7.1: Results from fitting equation (7.8) to spectra for low temperatures
Figure 7.6: (a)-(c) The temperature shifts of the NV\(^-\) spin, visible and IR resonances, respectively. The dashed lines represent the contribution of thermal expansion \(\Delta E_{ex}\) only; highlighting the importance of the electron-phonon \(\Delta E_{e-p}\) contribution.
CHAPTER 7. TEMPERATURE SHIFTS OF THE NV\textsuperscript{−} ENERGY LEVELS

Figure 7.7: Comparison of integral shown in equation (7.7) for small spherical nanoparticles of radius \( r \) as a function of temperature (\( T \)). The difference is due to the longest physical phonon wavelength being limited by particle size. The effect is exacerbated at low temperature because the population of long wavelength phonons is more significant.

Figure 7.7: Comparison of integral shown in equation (7.7) for small spherical nanoparticles of radius \( r \) as a function of temperature (\( T \)). The difference is due to the longest physical phonon wavelength being limited by particle size. The effect is exacerbated at low temperature because the population of long wavelength phonons is more significant.

frequency is \( \Omega_{\text{min}} = \nu_l/2\pi r \). For example, a 1 nm spherical nanoparticle has a minimum phonon frequency of \( \Omega_{\text{min}} \sim 1989 \text{ GHz} \) (8.2 meV). With a non-zero lower limit, the above integral no longer has an analytical solution. To check the significance of changing the lower phonon frequency limit, the integral was solved numerically with the \( a_{n,m,i} \) values determined from the \( b_{n,m,i} \) values that were found experimentally (see section 7.5). The results in figure 7.7 show that, at high temperature, the effect of the reducing particle size has no effect on the electron-phonon contribution. However, for very small particles (\( r \lesssim 10 \text{ nm} \)) at very low temperatures (\( T \lesssim 5 \text{ K} \)) there is a strong deviation from the bulk result. This occurs because more low frequency phonons are populated at lower temperatures resulting in a more significant effect when the lower frequency limit of the integral is increased. This has little or no practical implications as the temperature shift of the spin-resonances at these low temperatures is essentially flat, limiting the the thermometry applications of NV\textsuperscript{−} centres at very low temperatures.

7.5.3 Thermal expansion of diamond

There are alternative descriptions of the thermal expansion of diamond for different temperature ranges. In this analysis for temperature below 300 K, the polynomial description by Sato \textit{et al} [197] was used. For larger temperature ranges (0 K < \( T < \) 116
3000 K) the modal expansion of Reeb et al. [196] was used.

\[
\alpha = \sum_{n=0}^{4} \alpha_n T^n = 0.0, \alpha_1 = 4.10 \times 10^{-10}, \alpha_2 = -1.42 \times 10^{-11}, 1.46 \times 10^{-13}, \alpha_4 = -1.55 \times 10^{-16}. \]

The parameters for Reeb et al’s model are \( \theta_3 = 200, \theta_2 = 880, \theta_3 = 2137.5, X_1 = 0.4369 \times 10^{-7}, X_2 = 15.7867 \times 10^{-7}, X_3 = 42.5598 \times 10^{-7} \). As shown in figure 7.8(a), even in the overlapping temperature range \( T < 300 \) K there isn’t complete agreement of the two descriptions, possibly due to differing nitrogen concentrations. Note that to compare volumetric expansion using Sato et al’s expression for linear expansion, the relationship

\[
\ln \left( \frac{V + \Delta V}{V} \right) = 3 \sum_{i=1}^{3} \left( \frac{X_i \theta_i}{\exp \left( \frac{\theta_i}{T} \right) - 1} \right)
\]

(7.10)

Since the temperature shift model in equation (7.8) is a power series polynomial, the effect of impurity on thermal expansion should also be a power series. The model of Reeb et al was re-described using a power series that was truncated at the same maximum power. This was determined using least-squares fitting with very strong agreement (> 0.99999 correlation). Giving,

\[
\ln \left( \frac{V + \Delta V}{V} \right) = \sum_{n=1}^{5} \beta_n T^n, \quad (7.11)
\]

with coefficients \( \beta_1 = 1.3933 \times 10^{-7}, \beta_2 = -3.6391 \times 10^{-9}, \beta_3 = 2.8280 \times 10^{-11}, \beta_4 = -2.6690 \times 10^{-14}, \beta_5 = 8.8783 \times 10^{-18} \).

As shown in figure 7.8(b) the \( \Delta E_{ex} \) thermal expansion component of bulk diamond with different concentrations of nitrogen vary significantly. However, the resulting shift \( \Delta D \) is not greatly affected. This is due to the dominance of electron-phonon contribution to \( \Delta D \). This is convenient, as it allows the comparison of absolute temperature measurements from different samples with differing nitrogen concentrations. In particular, temperature comparisons are universally valid between high nitrogen samples which support dense ensembles of NV centres and low concentration high purity single site samples. As such, individual diamonds don’t need to be calibrated, which would be a nearly impossible task for a collection of nanodiamonds.

Sato et al [197] argues that the dominant effect of the change in the thermal expansion with varying nitrogen concentration is due to changes in the bulk modulus.
Figure 7.8: (a) Volumetric expansion of diamond from the models provided by Sato et al [197] and Reebet al [196]. (b) Comparison of the observed spin resonance shifts in bulk diamonds with different impurity nitrogen concentration [N]: green dashed, [N] < 1 ppm (observed by Chen et al [131]); blue dashed, [N] ∼ 0.4–4 ppm; and red dashed, [N] ∼ 40–60 ppm. The thermal expansion contribution to the spin resonance shift calculated using the thermal expansion coefficients of bulk diamonds with different nitrogen concentration [197]; black dashed - very low concentration, black dotted - high concentration [N] ∼ 78 ppm
B, they claim $B_{\text{Ni}}/B_{\text{high-purity}} \sim 1.23$. The effect of bulk modulus on the linear thermal expansion is

$$\alpha = \frac{\gamma C_V}{BV}, \quad (7.12)$$

where $C_V$ is the constant volume specific heat, $V$ is the volume and $\gamma$ is the Grüneisen’s parameter. Assuming the other parameters are fixed (as Sato et al. does), to first order small changes to the bulk modulus $\Delta B$ will result in a change to the thermal expansion coefficient $\Delta \alpha \propto \Delta B/B^2$. Note that it doesn’t make sense to simultaneously compare changes in the $B$ term in $\Delta E_{\text{ex}} = -a_1 BP(T)$, as it is describing the same effect. That is, the pressure required to overcome the incompressibility of material resisting change to thermal expansion. If the spin-mechanical susceptibility parameter $a_1$ was defined in terms of strain the $B$ term in the $\Delta E_{\text{ex}}$ expression would not be required.

Next, the effect of changing bulk modulus ($B$) on the electron-phonon contribution to the thermal resonance shift is considered. The density of modes $\rho(\omega)$ of the electron-phonon contribution $\delta(\omega)\rho(\omega)$ is given by

$$\rho(\omega) = \frac{V\omega^2}{2\pi^2 v^3}. \quad (7.13)$$

If it is assumed that changes in all terms of the stiffness tensor ($C_{11}, C_{12}, C_{44}$) are similar as nitrogen impurity increases. Then changes to the bulk modulus $B = (C_{11} + 2C_{12})/3$ are of similar order to changes in the speed of sound squared as $v_l(v_t) = \sqrt{C_{11}/\nu} (\sqrt{C_{44}/\nu})$, where $\nu$ is the material density and $v_l$ and $v_t$ are the longitudinal and transverse speeds of sound. Therefore the density of modes is $\rho(\omega) \propto 1/B^{3/2}$. A small change in $B$ will give a change to the density of modes $\Delta \rho(\omega) \propto \Delta B/B^{5/2}$. Considering only a change in $B$ with changing nitrogen concentration as Sato et al. argues, then the expected change in pressure due to the thermal expansion is larger than the change in phonon mode density, which affects the quadratic electron-phonon interaction. This validates the why the dominant electron-phonon contribution to the thermal isn’t strongly dependent on nitrogen concentration but the thermal expansion component is.

### 7.5.4 Full temperature range fit to the model

As previously discussed, the validity of the arguments that underpin the model as shown in equation (7.8) are questionable at temperatures much higher than room temperature. In particular, the requirement of only acoustic phonons mediating the
Table 7.2: Fit parameters for $b_4$ and $b_5$ for the $D$ shift and IR ZPL shift for the full useful NV$^-$ temperature range, from liquid He $\sim 5$ K up to $\sim 600$ K.

<table>
<thead>
<tr>
<th>Shift (Unit)</th>
<th>$\Delta D$ (MHz)</th>
<th>$\Delta E_{IR}$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b_4$ ($\text{Unit}/T^4$)</td>
<td>$-9.71(4) \times 10^{-10}$</td>
<td>$-4.8(8) \times 10^{-11}$</td>
</tr>
<tr>
<td>$b_5$ ($\text{Unit}/T^5$)</td>
<td>$1.27(1) \times 10^{-12}$</td>
<td>$2.4(1) \times 10^{-14}$</td>
</tr>
</tbody>
</table>

As shown in the spectra in figure 7.4(a), the visible ZPL is difficult to measure at high temperatures. This is due to a decrease in intensity relative to the large phonon sideband and ZPL broadening, for example only $4\%$ of emitting light is within the ZPL at room temperature. However, as shown in the spectra in figure 7.4(b), the infra-red ZPL has a smaller and less overlapped phonon sideband and does retain sharpness well above room temperature (a detectable ZPL was observed up to 500 K). The ODMR spectra shown in figure 7.3 shows that the $D$ shift is easily observable at high temperature. Toyli et al also demonstrated useful observable optical spin contrast up to temperatures of about 600 K [31].

The combined high and low temperature measurements are shown in figure 7.9. The fits are performed using the same model and only optimising the electron-phonon $b_4$ and $b_5$ parameters. The fitted parameters are shown in table 7.2. The thermal expansion component $\Delta E_{ex}$ was determined using the expression from Reeb et al [196];

$$\Delta E_{ex} = -a_1 B \frac{\Delta V}{V} = -a_1 B (e^{R(\beta,T)} - 1)$$  \hspace{1cm} (7.14)

where $R(\beta,T)$ is the expression for $\ln \left( \frac{V + \Delta V}{V} \right)$ given by Reeb et al in equation (7.10) or the polynomial approximation given in equation (7.11). The combined shift is simply

$$\Delta E = \Delta E_{ex} + \Delta E_{e-p} = -a_1 B (e^{R(\beta,T)} - 1) + \sum_{i=4}^{5} b_i T^i.$$  \hspace{1cm} (7.15)

This is the first time that the information from both the low and high temperature $D$ shift has been combined into a single expression. As shown in figure 7.10, the polynomial descriptions by Toyli et al ($T > 300$ K) and Chen et al ($T < 300$ K) do not give useful results in regions outside of their temperature range.
Figure 7.9: (a) Data points are IR ZPL shift and line is theoretical fit. The dashed lines again represent the $\Delta E_{ex}$ component only. (b) Data points are $D$ shift and line is theoretical fit. The dashed lines again represent the $\Delta E_{ex}$ component only.
CHAPTER 7. TEMPERATURE SHIFTS OF THE NV$^-$ ENERGY LEVELS

Figure 7.10: Disagreement of the polynomial descriptions of the $D$ shift by Toyli et al [31] and Chen et al [131] compared to the fit presented here over the full useful NV$^-$ temperature range.

7.6 Conclusion

By using a similar model to describe the energy shift of the optical transitions and the zero-field $D$ shift a self consistent explanation of the behaviour is obtained for the previously un-explained $D$ temperature shift. The temperature shift of the NV$^-$ IR ZPL is described for the first time. The only unknown parameters are the quadratic electron-phonon parameters which have been experimentally determined for both low and high temperature applications of the model. The dominance of the electron-phonon contribution over the thermal expansion component is significant, and allows for comparison of temperature to be made between multiple diamond samples of significantly differing nitrogen concentration. Finally, for the first time, data from the high and low temperature regimes were combined into a single expression for temperature shift of the $D$ and IR ZPL resonances from 4 K to 500 K.
CHAPTER 8

Temperature dependence of the $^{13}$C hyperfine interaction

8.1 Contributions

The experimental design and execution was performed by M.S.J. Barson and S. Yang. The data analysis was performed by M.S.J. Barson.

8.2 Introduction

As described in the previous chapter the temperature shift of the NV$^-$ spin resonance is due to the thermal expansion of the crystal lattice and temperature dependent electron-phonon processes. During thermal expansion/contraction or mechanical stress, the nuclei surrounding the NV$^-$ change position, causing the NV$^-$ electron orbitals to move and change. During this, not only are the electrons moving further apart (or together), but the unpaired electron spin-density spatial distribution is re-organising and changing. These processes are depicted in figure 8.1.

To probe the spatial change in spin-density, the hyperfine interaction of the $^{13}$C with the NV$^-$ $^3A_2$ ground state as a function of temperature is examined. This interaction is due to two contributions: (1) A dipolar interaction between the $^{13}$C nuclear spin and the electron spin of the NV$^-$; and (2) the Fermi contact interaction of the spin density at the $^{13}$C site. These two contributions are strongly dependent on the relative positions of the nuclei and electron orbitals. As such, the hyperfine interaction can be used as a atomscopic probe of the effect of thermal expansion on the NV$^-$ electrons.

If the interaction is significant, and given that nuclear T1/T2 times are much longer than electron spins, it is possible that the thermal dependence of the hyperfine interaction could also be exploited for high sensitivity thermometry.
CHAPTER 8. TEMPERATURE DEPENDENCE OF THE $^{13}$C HYPERFINE INTERACTION

Figure 8.1: Depiction of the stretching of the orbitals and changes in the spin-density due to crystal deformation. This deformation could be due to crystal stress or thermal expansion. The pink circles represent the change of location of the surrounding nuclei. The green circle represents the location of the vacancy.

8.3 Theoretical details

The hyperfine interaction of the NV$^-$ centre with the surrounding nuclei can be described by the following Hamiltonian,

$$H_{hf} = \vec{S} \cdot \vec{D} \cdot \vec{S} + \gamma_e \vec{S} \cdot \vec{B} + \vec{S} \cdot \vec{A} \cdot \vec{I} + \gamma_N \vec{I} \cdot \vec{B},$$  

(8.1)

where $\vec{S}$ are the spin-operators; $\vec{D}$ is the zero-field (or spin-spin) tensor; $\gamma_e$ is the electron gyromagnetic ratio; $\vec{B}$ is the applied magnetic field; $\vec{A}$ is the hyperfine tensor; $\gamma_N$ is the nuclear gyromagnetic ratio; and $\vec{I}$ are the nuclear spin operators. Although the nuclear Zeeman interaction is included in the last term, for the small magnetic fields ($B < 100$ G) used in this experiment the nuclear Zeeman effect can be neglected. This is because the $^{13}$C gyromagnetic ratio is $\gamma_n \approx 1$ kHz/G but the observable line width is $\Gamma_{ODMR} \approx 1$ MHz, preventing the nuclear Zeeman shifts from being observable. Changes in the terms within $\vec{A}$ as a function of temperature are of interest. In the diagonalised form there is only two components to $\vec{A}$, a component parallel and perpendicular to the NV axis $A_\parallel$ and $A_\perp$.
8.3. THEORETICAL DETAILS

\[ \hat{\mathbf{A}}_{\text{diag}} = \begin{pmatrix} A_\perp & 0 & 0 \\ 0 & A_\perp & 0 \\ 0 & 0 & A_\parallel \end{pmatrix}. \]  

(8.2)

The most widely accepted parameters are given by Felton et al [74] where, \( A_\parallel \) and \( A_\perp \) are 199.7(2) MHz and 120.3(2) MHz, respectively. However, these values are given in reference to the nuclear coordinate system at an angle \((\theta, \varphi) = (125.26^\circ, 45^\circ)\) from the crystallographic ([001],[010],[001]) coordinate system. This coordinate system is aligned along [111], which is at an angle \(\theta = \arccos\left(\frac{1}{\sqrt{3}}\right)\) from [111]. To convert to the NV spin coordinate system (where \(z\) is parallel to [111]) a rotation operation needs to be applied to the hyperfine tensor \( \hat{\mathbf{A}} = R \cdot \hat{\mathbf{A}}_{\text{diag}} \cdot R \). Ignoring the angle \(\varphi\) as the NV is axially symmetric about [111], the rotation matrix is,

\[ R = \begin{pmatrix} -\frac{1}{3} & 0 & \frac{2\sqrt{2}}{3} \\ 0 & 1 & 0 \\ -\frac{2\sqrt{2}}{3} & 0 & -\frac{1}{3} \end{pmatrix}. \]  

(8.3)

This rotation gives the hyperfine tensor,

\[ \hat{\mathbf{A}} = \frac{1}{9} \begin{pmatrix} 8A_\parallel + A_\perp & 0 & -2\sqrt{2}A_\parallel + 2\sqrt{2}A_\perp \\ 0 & A_\perp & 0 \\ -2\sqrt{2}A_\parallel + 2\sqrt{2}A_\perp & 0 & A_\parallel + 8A_\perp \end{pmatrix}. \]  

(8.4)

In the perturbative picture which assumes that the hyperfine energies are much less than the spin-spin energies (i.e. \( D \gg A \)), to first-order the hyperfine split energy levels are simply the eigenvalues of the hyperfine interaction within the \( S_z \) spin sub-space,

\[ \text{Eigenvalues} \left( \sum_{i=1}^{3} \tilde{I}_i \hat{A}_i, S_z \right) \]  

(8.5)

Using the spin \(-1/2\) Pauli matrices for \( I_x = \sigma_x/2 \) and \( I_z = \sigma_z/2 \) gives the hyperfine resonances,

\[ \Delta = \pm \frac{m_s}{6} \sqrt{A_\parallel^2 + 8A_\perp^2}. \]  

(8.6)

\[ \Delta = \pm \frac{m_s}{6} \sqrt{A_\parallel^2 + 8A_\perp^2}. \]  

(8.7)
CHAPTER 8. TEMPERATURE DEPENDENCE OF THE $^{13}$C HYPERFINE INTERACTION

Substituting in the hyperfine parameters from Felton et al [74] gives a relative shift of the form $\Delta = \pm 65.7$ MHz. This large $\sim 130$ MHz splitting enables the easy identification of NV$^-$ centres with a first shell $^{13}$C.

The hyperfine terms can be described by the Fermi contact term $f$ and the dipolar term $d$ [76],

$$A_\parallel = f + d$$
$$A_\perp = f - 2d.$$  \hspace{1cm} (8.8)

For a perfectly spherical distribution ($s$–orbital) of unpaired electrons there is no dipolar term, requiring some $p$–, $d$– or $f$–orbital character. The contact interaction is spatially isotropic and requires non-zero probability that the electron is at the $^{13}$C nucleus, these conditions are satisfied by an $s$–orbital. Using these arguments, a hybrid orbital $\psi$ that is a linear combination of $s$– ($\phi_s$) and $p$–orbitals ($\phi_p$) can be constructed [76],

$$\psi = c_s \phi_s + c_p \phi_p$$
$$1 = |c_s|^2 + |c_p|^2,$$  \hspace{1cm} (8.9)

the Fermi contact $f$ and dipolar terms $d$ can be described using the orbital $\psi$ as [91],

$$f = \frac{8\pi \mu_0}{3} \frac{\mu_B g_n \mu_N}{4\pi} |c_s|^2 \eta |\phi_s(0)|^2$$  \hspace{1cm} (8.10)
$$d = \frac{2\mu_0}{3} \frac{\mu_B g_n \mu_N}{4\pi} |c_p|^2 \eta \langle \phi_p | \frac{1}{r^3} | \phi_p \rangle,$$  \hspace{1cm} (8.11)

where $|\phi_s(0)|^2$ is the probability per unit volume of $s$–orbital at the location of the $^{13}$C nucleus and $\langle \phi_p | \frac{1}{r^3} | \phi_p \rangle$ is the average $1/r^3$ value of the $\phi_p$ orbital. These values are numerically determined and available in published tables [204, 205, 206]. $\eta$ is the electron spin-density at the nucleus, $g_n$ is the $^{13}$C nuclear $g$–factor and $\mu_N$ is the nuclear magneton. These relationships show that measuring $A_\parallel$ and $A_\perp$ to determine $f$ and $d$ allows for the determination of the temperature dependent changes to the NV$^-$ orbital hybridisation $|c_s|^2 / |c_p|^2$ and the spin-density $\eta$. He et al [91] used these methods to determine the hybridisation of the NV$^-$ as $|c_s|^2 / |c_p|^2 = 9.0$, which is strongly changed from the conventional $sp^3$ hybridisation ratio of $0.75/0.25 = 3$ and represents a change in bond angle from 109.5° to 96.4°. Similarly Felton et al [74] used these methods and found that 84% of the unpaired spin-density was located at the three nearest carbons.

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By applying a magnetic field that is perpendicular and parallel to the NV\textsuperscript{−} axis differing components of \(S_x\), \(S_y\) or \(S_z\) can be measured. These components couple differently to the nuclear spin allowing for \(A_{\parallel}\) and \(A_{\perp}\) to be uniquely determined. In the low-field limit, this must be done by sweeping the magnetic field and angle as each direction gives a mixture of \(A_{\parallel}\) and \(A_{\perp}\) contributions. However, at high field, using the secular approximation, the quantisation axis of the spins change to the magnetic field direction and the \(A_{\parallel}\) and \(A_{\perp}\) can be determined from spectra by modifying field angle alone. It may be possible to measure \(A_{\perp}\) by applying a very well aligned axial field at the ground state level-anti crossing (GSLAC, 1025 G) as the voided crossing energy is due transverse magnetic fields such as the hyperfine \(A_{\perp}\) interaction [100].

8.4 Experimental details

For high temperature measurements a diamond with a dense NV\textsuperscript{−} ensemble was used. The sample used here was the same as described in chapter 4.3. For the ODMR detection a lock-in amplifier (Femto LIA-MV-200) was used. The microwave signal was chopped using a switch with a square wave TTL reference signal at \(~\text{100}\text{s}\) of Hz. The increased sensitivity from the lock-in amplifier allowed for \(^{13}\text{C}\) ODMR resonances to be easily measured above background noise, even for the relatively low \(~\text{1}\%\) natural abundance of \(^{13}\text{C}\) expected in the ensemble, as shown in figure 8.2. For high temperature the same experimental ODMR hotplate apparatus was used as described in chapter 7.

For low temperature, single site \(^{13}\text{C}\) measurements a liquid helium cold finger continuous flow cryostat was used with a scanning confocal microscope. A 0.9 NA Nikon LU Plan Fluor air objective was mounted on a 3 axis piezo scanning stage within the vacuum space of the cryostat. Microwaves were provided to the sample via a 25 \(\mu\text{m}\) wire soldered across the sample. Since single NV centres with an adjacent first shell \(^{13}\text{C}\) were required, an alpha-numerical grid and marker system was scribed into the diamond using FIB. This allowed for a particular NV to be found repeatedly. Due to the low probability of finding a single NV centre with a \(^{13}\text{C}\) in the first shell, a search algorithm was employed that recorded the position of bright spots and performed CW ODMR at each bright spot to establish if that bright spot was an NV centre with a first shell \(^{13}\text{C}\).
Figure 8.2: Example of $^{13}\text{C}$ ODMR spectra from an ensemble of NV$^-$ centres when using a lock-in amplifier on the microwave signal. The upper/lower plots are from lower/higher gain on the lock-in amplifier. The prominence of the usually insignificant $^{13}\text{C}$ hyperfine peaks on the lower plot demonstrates the considerable enhancement of signal to noise. The signal from the central resonance saturates the lock-in amplifier at high gain. This spectra was taken at $T = 180$ °C.
8.5 Results and analysis

The $^{13}$C ODMR spectra were fitted using the model $I$ where $B$ represents the lineshape function, either a Gaussian ($G$) or a Lorentzian ($L$).

\[
I = B(\omega; D, K, A_1, \sigma_1) + B(\omega; D, -K, A_2, \sigma_2) \tag{8.12}
\]

\[
G(\omega; D, K, A, \sigma) = \frac{A}{\sqrt{2\pi}\sigma^2} e^{-\frac{(\omega - (D+K))^2}{2\sigma^2}}
\]

\[
L(\omega; D, K, A, \Gamma) = \frac{A}{\pi} \left( \frac{1}{2\Gamma} \right)^2 \frac{1}{\left( \frac{\omega - (D + K)}{\Gamma} \right)^2 + \left( \frac{1}{2\Gamma} \right)^2} \tag{8.13}
\]

When fitting this model to the spectra from an ensemble of NV$^-$ centres, the central ODMR peak was ignored and only the $^{13}$C components of the spectra were included. The $^{13}$C components of the spectra can be seen as the two peak split by $\sim 130$ MHz either side of the main resonance at 2.87 GHz as shown in figure 8.3(b). As such, $D$ is expected to be approximately 2.87 GHz and $2K$ to be approximately 130 MHz. The lineshapes used when fitting ODMR spectra from single NV$^-$ centres are Lorentzian and Gaussian when fitting to the spectra from ensembles due to inhomogeneous broadening. In either case, the results are similar since only the central position (and not width or amplitude) of the resonances are relevant for this measurement.

The resulting temperature dependence of the $^{13}$C hyperfine interaction was shown to be constant with changing temperature. For experiments conducted at both both low and high temperature with ensembles and single NVs, the two resonances mean position followed the already defined temperature $D$ shift closely, as shown in figure 8.3(c). However, the difference ($2K$) between the two resonance did not change significantly ($< 100$ kHz) as shown in figure 8.3(d). There is a small offset in both the mean and difference of the spin-resonances, this is likely due to a small difference in magnetic field ($< 5$ G). These samples were performed on very different samples (one single NV low N concentration and the other an irradiated high N concentration) using completely different experimental set-ups. It is possible that some small magnetisation could be present in one experiment and not the other. This difference in magnetisation would present itself as the change in the difference and mean positions of the spin-resonances (for a transverse magnetic field).

Since there was no significant change with zero applied field, it was decided not to pursue field alignment and field sweeping to separate the $A_{\parallel}$ and $A_{\perp}$ terms.

Despite the change being small, these results can be used to infer an upper limit
CHAPTER 8. TEMPERATURE DEPENDENCE OF THE $^{13}$C HYPERFINE INTERACTION

Figure 8.3: (a) Example ODMR spectra from a single NV$^-$ centre with a $^{13}$C in the first shell of carbons, taken at $T = 15$K. (b) Example ODMR spectra from an ensemble of NV$^-$ centres with the $^{13}$C hyperfine resonances clearly visible either side of the main spin resonance. The main resonance is assumed to split due to a small remnant magnetic field or crystal strain. (c-d) The temperature shifts of $D$ and $2K$, according to the fitting model in equation (8.12). The $D$ shift follows the expected trend described in chapter 7, $K$ shows no obvious change. The high temperature data (red) is an ensemble and the low temperature (blue) is from a single NV centre with first shell $^{13}$C. The larger error bars for the ensemble are due to inhomogeneous broadening and larger resonance line-widths. The small offset for the absolute value for the $D$ and $2K$ between the two data sets is probably also due to some small change in transverse magnetic fields ($< 5$ G). The two data sets come from experiments that were performed on different samples, equipment and continents.
on changes in the electron orbitals. A maximum change of \( \sim 100 \text{ kHz} \) due to the observed experimental fluctuations is observed. Using this, the upper limit in the change of NV\(^-\) spin density \( \eta \) at the \( ^{13}\text{C} \) can be determined. The zero-field hyperfine splitting is given by equation (8.6) as,

\[
A_{\text{zfs}} = \frac{1}{6} \sqrt{A_\parallel^2 + 8A_\perp^2},
\]

substituting in the expressions for \( f \) and \( d \) given in equation (8.8),

\[
A_{\text{zfs}} = \frac{1}{6} \sqrt{(f + d)^2 + 8(f - 2d)^2}, \quad (8.14)
\]

Assuming that only the spin density changes and all other parameters remain constant, the effect on \( A_{\text{zfs}} \) is then,

\[
\Delta A_{\text{zfs}} = \Delta \eta \left( \frac{\partial A_{\text{zfs}}}{\partial f} \frac{\partial f}{\partial \eta} + \frac{\partial A_{\text{zfs}}}{\partial d} \frac{\partial d}{\partial \eta} \right) \bigg|_{A_\parallel, A_\perp, \eta}. \quad (8.15)
\]

Using an upper bound on the change in the zero-field splitting of \( \Delta A_{\text{zfs}} \approx 500 \text{ kHz} \) and substituting the parameters \( \mu_N = 5.05 \times 10^{-27} \text{ J/T} \), \( \mu_B = 9.27 \times 10^{-24} \text{ J/T} \), \( g_n = 1.404 \), \( g_e = 2.0 \), \( |c_s|^2 = 0.1 \), \( |c_p|^2 = 0.9 \), \( \eta = 0.24 \) \cite{91}, \( \langle \phi_p | \frac{1}{r} | \phi_p \rangle = 2.02a_0^3 \text{ m}^3 \), \( |\phi_s(0)|^2 = 1.69a_0^3 \text{ m}^3 \) \cite{204} gives the upper bound on the change in \( \eta \) of \( \Delta \eta \approx 0.5\% \). Considering the spin density at the \( ^{13}\text{C} \) has been previously been shown to be 24\% \cite{91}, this result shows a negligible change in the spin-density due to the expansion of the diamond.

### 8.6 Conclusion

When describing the spin-mechanical behaviour in chapter 3, it was argued that the NV\(^-\) \( D \) shift during crystal expansion or contraction was due to two effects: (1) the orbitals changing; and (2) that the spin-density re-distributing in between atoms. The \( ^{13}\text{C} \) hyperfine interaction was used to probe these effects. Since no change in the hyperfine interaction is observed, the spin-density at the \( ^{13}\text{C} \) does not change as the crystal expands. Similarly, the orbitals do not change hybridisation, implying no reorientation of the bonds. To explain this result, the electron orbital must exactly follow the carbon nuclei as the crystal expands. This is the first atomscopic measurement of changes to the NV\(^-\) centres’ orbitals due to the deformation of the surrounding crystal.

Given that the change in the interaction due to temperature is weak or non-
existential, there is no scope for improved thermometry by taking advantage of the hyperfine interaction despite the improved coherence times of the nuclear spins.
9.1 Contributions

The experimental design and execution was performed by E. Krausz. The data analysis and interpretation was performed by M.S.J. Barson, N.B. Manson and M.W. Doherty.

9.2 Introduction

This chapter studies the results from magnetic circular dichroism (MCD) measurements of the optical transition of the NV⁻ infra-red ZPL emission between the $^1A \rightarrow ^1E$ levels and the NV⁰ ZPL absorption between the $^2E \rightarrow ^2A_2$ levels. The orbital magnetic properties of the singlet $^1E$ are determined for the first time. The fine structure of the NV⁰ $^2E$ and $^2A_2$ levels are observed and analysed for the first time.

9.3 Theoretical details

MCD is a type of spectroscopy that determines the difference in absorption of left and right circularly polarised light in the presence of a large magnetic field parallel to the light propagation. This difference in absorption is due to the degeneracy of optical transitions being lifted by the magnetic field, for transitions that have different left and right circularly polarised selection rules. Using fast modulation of left and right circularly polarised light and lock-in techniques, small splittings in excited or ground state energy levels which are much smaller than the observable
Figure 9.1: Depiction of total absorption and MCD signal due to non-degenerate circularly polarised levels. The MCD signal is the difference of the left and right circularly polarised components of absorption. The signal is measured using a fast differential lock-in technique. As the monochromator is swept the photo-elastic modulator and chopper wheel with lock-in amplifiers measure the left $I_\uparrow$, the right $I_\downarrow$ and total signal simultaneously.

Linewidth can be detected. In fact, due to the differential line shape of the signal, spectral features much smaller than the spectral resolution of the monochromator can be identified. For example, conventional high resolution monochromators have a spectral resolution $\sim 0.01\ \text{nm (} \sim 6\ \text{GHz at 700 nm)},$ but the MCD signal can reveal features within $< 100\ \text{MHz}$ resolution. The MCD signal is not specifically dependent on spin state, as the optical selection rules do not differentiate between different spin levels. However, the experiments are generally performed at low temperature and large magnetic field where the thermal polarisation of the lower Zeeman split spin branch is significant. As such, the measurements are sensitive to differences in the orbital states and the thermal polarisation of the ground state. Given this, information such as the spin-orbit, spin and orbital $g$-factors and mixing between near degenerate states can be extracted. In the following discussion and for the remainder of the chapter the spin states are designated with $+1, -1, 0$ or just $\pm$ and the orbital states with $\uparrow, \downarrow$.

Using the Beer-Lambert law, the attenuation of light through an absorbing medium of length $L$ is given as,

$$\frac{dI}{I} = -\kappa dL, \quad (9.1)$$
which can be solved as
\[ \log_{10} \left( \frac{I}{I_0} \right) = \kappa(\nu)L = Z, \quad (9.2) \]

where \( \kappa(\nu) \) is the absorption coefficient that is, in general, strongly dependent on frequency \( \nu \), \( I_0 \) is the incident intensity and \( Z \) is the absorbance in \( \log_{10} \) units. Defining the absorption coefficient to consist of components which absorb left (\( \kappa_\downarrow \)) and right (\( \kappa_\uparrow \)) circularly polarised light gives the total absorption coefficient and the differential absorption coefficient \( \Delta \kappa \)
\[
\kappa(\nu) = \kappa_\downarrow(\nu) + \kappa_\uparrow(\nu) \quad (9.3)
\]
\[
\Delta \kappa(\nu) = \kappa_\downarrow(\nu) - \kappa_\uparrow(\nu). \quad (9.4)
\]

The absorption coefficients \( \kappa_\uparrow\downarrow(\nu) \) are due to light being absorbing by circularly polarised electric-dipole transitions between ground (\( a \)) and excited states (\( j \)). As such, using expressions from Piepho and Schatz [207], \( \kappa_\uparrow\downarrow(\nu) \) can be written as
\[
\kappa_{a\uparrow\downarrow}(\nu) = \frac{8\pi^3 \nu \alpha^2}{\hbar \epsilon n} N_a |\langle a|m_{\uparrow\downarrow}|j \rangle|^2 \mathcal{L}_{a\uparrow\downarrow}(\nu), \quad (9.5)
\]
where \( N_a \) is the number of absorbers in the \( a \) state, \( \alpha \) is the effective field correction constant, \( n \) is the refractive index, \( m_{\uparrow\downarrow} \) is the electric dipole operator for left/right circularly polarised light and \( \mathcal{L}_{a\uparrow\downarrow} \) is the lineshape function of the transition.

The absorption \( (Z) \) of the sum of the two polarisation components due to the absorber can be given as,
\[
Z_{L+R}(E) = (\kappa_\downarrow + \kappa_\uparrow) L \quad (9.6)
\]
\[
\frac{Z_{L+R}(E)}{E} = \gamma \sum_{a\downarrow} \frac{N_a}{N} (|\langle a|m_\downarrow|j \rangle|^2 + |\langle a|m_\uparrow|j \rangle|^2) \mathcal{L}_{a\downarrow}(E), \quad (9.7)
\]
where the signal has been divided by \( E = h\nu \) and \( \gamma \) is a collection of spectroscopic constants. The signal is divided by \( E = h\nu \) because the absorption is \( \propto \nu \), ensuring the linearity of the absorption signal. The constants in \( \gamma \) are in principle known, but since the MCD analysis presented here always takes the ratio of two spectra the details of \( \gamma \) are not required. The sum is performed over all allowed transitions between multiple available ground and states (\( a \rightarrow j \)). Similar to the total absorption
CHAPTER 9. MAGNETIC CIRCULAR DICHR OISM OF THE NV CENTRE’S FINE STRUCTURE

the differential absorption is

\begin{align}
Z_{L-R}(E) &= \Delta \kappa = (\kappa_\downarrow - \kappa_\uparrow) L \\
\frac{Z_{L-R}(E)}{E} &= \gamma \sum_{a_j} \frac{N_a}{N} \left( |\langle a|m_\downarrow|j\rangle|^2 - |\langle a|m_\uparrow|j\rangle|^2 \right) \mathcal{L}_{a_j}(E).
\end{align}

(9.8)

(9.9)

Next the rigid shift approximation is applied, this assumes that the lineshape function is translated by a magnetic Zeeman shift ($\delta$) but doesn’t change shape. i.e. $\mathcal{L}(E) \rightarrow \mathcal{L}(E - \delta)$. Re-describing the dipole strengths $|\langle a|m_\downarrow|j\rangle|^2 = \sigma_{a\downarrow j}$ and the number of available ground state absorbers $N_a/N$ with a probability $P_a$ allows for the total absorption and differential absorption to be written as,

\begin{align}
\frac{Z_{L+R}(E)}{E} &= \gamma \sum_{a_j} P_a (\sigma_{a\downarrow j} \mathcal{L}(E - E_j - E_a) + \sigma_{a\uparrow j} \mathcal{L}(E - E_j - E_a)) \\
\frac{Z_{L-R}(E)}{E} &= \gamma \sum_{a_j} P_a (\sigma_{a\downarrow j} \mathcal{L}(E - E_j - E_a) - \sigma_{a\uparrow j} \mathcal{L}(E - E_j - E_a)).
\end{align}

(9.10)

(9.11)

A diagram depicting the electronic energy levels and the addition and subtraction of the bands can be seen in figures 9.1 and 9.2.

In general, fitting a parametric lineshape curve to MCD spectra can sometimes be difficult. This difficulty can arise if the absorption through the solid doesn’t result in a truly Gaussian functional shape or there are too many free parameters in the fit and the function is not constrained enough by the spectra. This can often be true for MCD signals as the separation of the two left and right circularly polarised lines is much smaller than the linewidth, as shown in figure 9.2. Fortunately, the relevant information in the MCD spectra can also be extracted from the spectral moments. Although originally described by Lax [208], it was Henry, Schnatterly and Slichter [209] who pioneered the use of moments for analysing MCD spectra. For an absorption band $f(E)$ the total area of the band or zeroth moment is

\[ I = \int_{-\infty}^{+\infty} f(E)dE, \]

(9.12)

which is used to determine the centroid of the band

\[ \bar{E} = \frac{1}{I} \int_{-\infty}^{+\infty} Ef(E)dE. \]

(9.13)

This centroid is used as the central position of the band for which the higher order
9.3. THEORETICAL DETAILS

Figure 9.2: Simulated absorption (plotted here as $A$ normalised to $A_{\text{max}}$) and MCD (difference in left and right absorption $\Delta A$ also normalised to $A_{\text{max}}$) signals for a Gaussian absorption with width $w$ and varying separation $\Delta E$ between the two lines. Since the separation is much smaller than the line width the sum of the two lines completely overlap. However, the difference of the two lines gives a differential shape. The vertical scale is the same for both plots.
(n ≥ 1) moments are determined about. As such,
\[
\langle E \rangle^n = \frac{1}{I} \int_{-\infty}^{+\infty} (E - \bar{E})^n f(E) dE.
\] (9.14)

For the centroid and moments to be numerically accurate, the band line shape must go to zero on either side \( f(E \to \pm\infty) \to 0 \), this is enforced for our spectra by background subtraction.

In the following results, both lineshape fitting and moment analysis were applied simultaneously to cross validate the results. When fitting, functions of the form shown in equations (9.10) and (9.11) were simultaneously applied to the absorption and MCD spectra. The fitting of both spectra was simultaneously performed by optimising the combined least-squares from both spectra. Lineshape functions were chosen to be Gaussian as this signal was from an ensemble of centres and inhomogeneous broadening is assumed to be the dominant broadening mechanism.

The comparison between the fitted parameters and the moments is simply
\[
\frac{\langle Z_{L-R} \rangle_1}{\langle Z_{L-R} \rangle_0} = d \text{ (GHz)}
\] (9.15)
\[
\frac{\langle Z_{L-R} \rangle_0}{\langle Z_{L-R} \rangle_0} = \frac{A_1 - A_2}{A_1 + A_2},
\] (9.16)

where \( 2d \) is the separation between two lineshapes of amplitude \( A_1 \) and \( A_2 \). For example, using Gaussian lineshapes,
\[
\frac{Z_{L-R}}{E} = \frac{A_1}{\sqrt{2\pi}\sigma^2} \exp\left(-\frac{(E - \mu - d)^2}{2\sigma^2}\right) - \frac{A_2}{\sqrt{2\pi}\sigma^2} \exp\left(-\frac{(E - \mu + d)^2}{2\sigma^2}\right)
\] (9.17)
\[
\frac{Z_{L+R}}{E} = \frac{A_1}{\sqrt{2\pi}\sigma^2} \exp\left(-\frac{(E - \mu - d)^2}{2\sigma^2}\right) + \frac{A_2}{\sqrt{2\pi}\sigma^2} \exp\left(-\frac{(E - \mu + d)^2}{2\sigma^2}\right).
\] (9.18)

When fitting the above functions to the differential and absorption spectra the free parameters were the amplitudes \( A_1 \) and \( A_2 \), mean position \( \mu \), width \( w \) and separation \( d \). The spectra were fitted simultaneously with only the previous five values free across both spectra (plus constant background offsets). Due to the difference in scale of the differential and total absorption signals and the fact that they were simultaneously optimised, the sum of squares of the residuals for the differential part was weighted so that the residuals were a similar size to the total absorption residuals.

To determine the uncertainty in the measured value of the spectral moments a bootstrap Monte-Carlo method was adopted. The variance of the noise (\( s^2 \)) in the
9.4 EXPERIMENTAL DETAILS

detected photocurrent away from the central band was measured. Assuming that
the noise is Gaussian and wavelength independent i.e. \( S' = S + N(0, s) \), where \( S \) and
\( S' \) are the true and measured photocurrents, respectively and \( N(0, s) \) is normally
distributed noise with variance \( s^2 \). The uncertainty in the moments was determined
using a bootstrap Monte-Carlo method that repeatedly modulated the raw spectra
by \( N(0, s) \) and recalculated the spectral moments. This was done separately for the
MCD and absorption spectra. The uncertainty was taken as the standard deviation
of the resultant distribution of spectral moments produced from the bootstrap. The
wavelength uncertainty was assumed to be negligible compared to the photocurrent
signal noise. The temperature and magnetic field uncertainties were taken from the
measurement error and incorporated into the above bootstrap routine by modulating
the variable by normally distributed random noise with a standard deviation equal
to the experimental error. Similarly, to determine the error in the curve fitting
the signal was modulated by normally distributed noise with a standard deviation
equal determined from the residuals of the initial fit. The fit sequence was re-run
repeatedly and the resulting distribution of fit parameters used to determine the
standard error of the parameters. In general, this resulted in a smaller uncertainty
for the spectral moments than for the curve fitting. This is simply because no model
or particular result is expected from the moments and the experimental photocurrent
noise can be very small. Consequently, by not applying a model any unknown
systematic errors aren’t excluded and can be reflected in the final result. Conversely,
the curve fitting method applies a model and bases the uncertainty in the results on
how well that model succeeds. As such, the uncertainty can be higher but systematic
errors are more likely to be rejected by the model. Because of the pros and cons of
each method they were both performed independently for cross validation.

9.4 Experimental details

The experiments were performed by Prof Elmars Krausz at the Research School
of Chemistry, Australian National University. Prof Krasuz has perfected the MCD
spectroscopy technique over his career and has a dedicated MCD spectroscopy lab.
A more detailed report of the experimental equipment and methods can be seen in
references 210 and 211. The main experimental configuration is shown in figure 9.3.

The NV\(^-\) IR measurements were performed on the same \( 2 \times 2 \times 2 \) mm\(^3\) cu-
bic samples from the uniaxial mechanical measurements in chapter 4. The sample
preparation is described in chapter 4, this treatment resulted in dense ensembles of
NV\(^-\) centres that were visible by eye using using a conventional 100 mW 532 nm
The ANU optical spectrometer system, as configured for wide-band, multi-wavelength micro-photoluminescence studies on photosynthetic samples. The ANU optical spectrometer system, as configured for wide-band, multi-wavelength micro-photoluminescence studies on photosynthetic samples.
9.5 Results and analysis

Two sets of MCD measurements were performed on the NV centre: (1) the IR ZPL transition of NV\textsuperscript{−} (\textsuperscript{1}A\textsubscript{1} ↔ \textsuperscript{1}E); and (2) the visible ZPL of NV\textsuperscript{0} (\textsuperscript{2}A\textsubscript{2} ↔ \textsuperscript{2}E).

9.5.1 NV\textsuperscript{−} infra-red zero-phonon line

Theoretical description

In the case of the IR ZPL transition, the only magnetic response is the Zeeman splitting of orbital states of the \textsuperscript{1}E level. The \textsuperscript{1}A\textsubscript{1} level is an orbital singlet and a spin singlet, so there is no magnetic response. Since both levels are spin singlets, all spin-orbit and spin Zeeman effects are not applicable. The energy levels of the \textsuperscript{1}E state are Zeeman split by $\Delta_{\uparrow\downarrow} = \pm l \mu_B B_z$, where $l$ is the orbital $g$-factor. Since absorption of the meta-stable singlet states is difficult [67] this spectra was actually taken in emission not absorption. Absorption measurements are difficult because the singlet levels are metastable states that must be continuously pumped by exciting the NV\textsuperscript{−} with a 532 nm laser. This means the absorption measurements have to be done in a two light source pump-probe fashion, as such MCD in emission was chosen for experimental simplicity. The excitation laser was carefully polarisation scrambled so the left and right circularly polarised emissions have equal probability. However, the laser is only there to pump the visible transmission. The system goes through the inter-system crossing to the \textsuperscript{1}A state before infra-red emission so no character of the excitation laser is preserved before the relevant emission in the singlet states.
Figure 9.4: MCD emission of the NV− IR ZPL, the left and right circularly polarised emission are given by the red and blue arrows.

The previous arguments of the optical selection rules and analysis of the absorption spectra is exactly the same for emission. The relevant dipole strengths between the excited and ground states are $\sigma^\uparrow$ and $\sigma^\downarrow$. Labelling the energy levels as $E_A$, $E_\downarrow$ and $E_\uparrow$, the emission band is,

$$\frac{Z_{L+R}(E)}{E^3} = C_{\text{TOT}} (\sigma^\downarrow \mathcal{L} (E_\downarrow - E_A - E) + \sigma^\uparrow \mathcal{L} (E_\uparrow - E_A - E)), \quad (9.19)$$

where $C_{\text{TOT}}$ is a constant which contains information about the total emission strength. For emission the spectra is divided by $E^3 = (h\nu)^3$, unlike absorption which was divided by $E$. This is because the emission strength is essentially the Einstein spontaneous emission rate which is $\propto \nu^3$ [212]. As with absorption this scaling is required to ensure linearity of the absorption but its effect is fairly minimal over such a small wavelength range. Similarly, the differential emission signal will be,

$$\frac{Z_{L-R}(E)}{E^3} = C_{\text{MCD}} (\sigma^\downarrow \mathcal{L} (E_\downarrow - E_A - E) - \sigma^\uparrow \mathcal{L} (E_\uparrow - E_A - E)). \quad (9.20)$$
Applying moment analysis the total area of the band is,

\[ I = \int_{-\infty}^{+\infty} \frac{Z_{L+R}(E)}{E^3} dE = C_{\text{TOT}} (\sigma_\downarrow + \sigma_\uparrow). \]  

(9.21)

The centroid of the band is then,

\[ \bar{E} = \frac{1}{I} \int_{-\infty}^{+\infty} E \frac{Z_{L+R}(E)}{E} dE \]

(9.22)

\[ = \frac{1}{2} \left( (E_\downarrow - E_A) + (E_\uparrow - E_A) \right), \]

the average energy difference between the excited and ground states. The zeroth spectral moment of the band is \( \langle \frac{Z_{L+R}}{E^3} \rangle_0 = C_{\text{TOT}} (\sigma_\downarrow + \sigma_\uparrow). \) The first spectral moment of the MCD signal is \( \langle \frac{Z_{L+R}}{E^3} \rangle_1 = C_{\text{MCD}} (\sigma_\downarrow E_\downarrow - \sigma_\uparrow E_\uparrow). \) The energy levels of the ground states are simply \( E_{\downarrow \uparrow} = \pm g_l \mu_B B_z. \) The transition strengths \( |\langle A|\sigma_\downarrow \downarrow \rangle|^2 = |\langle A|\sigma_\uparrow \uparrow \rangle|^2 \) [207], are equal \( \sigma_\downarrow = \sigma_\uparrow \), giving the ratio of the moments,

\[ \frac{\langle \frac{Z_{L+R}}{E^3} \rangle_1}{\langle \frac{Z_{L+R}}{E^3} \rangle_0} = \frac{C_{\text{MCD}} g_l \mu_B B_z}{2C_{\text{TOT}} \sigma_\downarrow} \]

(9.23)

Gaussians as shown in equations 9.17 and 9.18 were also fitted to the spectra. Using equation (9.15) the separation of the two Gaussians can be compared to the ratio of moments giving \( d = g_l \mu_B B_z. \)

**Results and analysis**

The ratio of moments is shown in figure 9.5(b), the gradient of which is \( \mu_B l \cos \theta = 0.251(1) \) GHz/T using the values from curve fitting, \( \mu_B l \cos \theta = 0.208(4) \) GHz/T using the values from spectral moment and \( \mu_B l \cos \theta = 0.230(3) \) GHz/T from the average of the two. Since the magnetic field is aligned along the \( \langle 100 \rangle \) direction the field projection along the NV axis is \( B_z = B \cos \theta \) with \( \cos \theta = 1/\sqrt{3}. \) Using the average gradient above, gives an orbital \( g \)-factor of \( l = 0.028 \pm 0.004 \), to our knowledge, this is the first time this parameter has been measured.

The orbital \( g \)-factor found here is significantly reduced from the free atom value of \( l = 1 \) or the experimentally determined NV\(^-\) excited \( ^3E \) state values. The only measurements of the orbital \( g \)-factor of the \( ^3E \) are by Reddy et al who found \( l = 0.1 \) by performing MCD [47] and by Hanzawa et al [148] who measured a \( l = 0.2 \) from the Zeeman shift of the NV\(^-\) ZPL directly using very large magnetic fields. It is expected from the electronic model of the NV centre that the \( ^1E \) orbital \( g \)-factor
Figure 9.5: (a) Example of MCD differential emission spectra (upper) and total emission spectra (lower) for the IR ZPL of NV$^-$ at a temperature of 1.46 K, notice the sign change due to magnetic field. Fits are of the form shown in equations 9.11 and 9.10 using Gaussian lineshape functions. (b) Zeeman shift of $^1E$ orbitals determined the separation of two Gaussian fits (points) and from spectral moments (stars) vs $B$, where $B \parallel [100]$, line is simple linear fit.
9.5. RESULTS AND ANALYSIS

Figure 9.6: Depiction of the linear Jahn-Teller interaction between an $E$ electronic level and single $E$ and $A$ phonons. The linear Jahn-Teller interaction of an $E$ electronic state with an $E$ phonon $E \otimes E = E \oplus A_1 \oplus A_2$ vibronic levels. A further quadratic interaction will break the degeneracy of the $A_1$ and $A_2$ levels. Note that $E \otimes A_1 = E$, so interactions with symmetric $A_1$ phonons do not introduce new levels. The linear energy separation of the $A_1$ and $A_2$ levels from the $E$ level is $\Delta$ and the quadratic splitting of the $A_1$ and $A_2$ levels is $\delta$. The application of transverse strain slightly mixes the $A_1$ and $E$ levels such that the $A_1$ level becomes apparent in emission.

should be twice that of the $^3E$ orbital $g$–factor. This is because in the $^1E$ level, two holes occupy the $e$ orbitals ($e^2$), whereas in the $^3E$ one hole occupies the $e$ and other hole occupies the $a$ orbital, which has no angular momentum [75, 213]. To explain the loss of angular momentum, a Ham reduction factor from a dynamic Jahn-Teller interaction is assumed [145]. The Ham reduction is a consequence of the mixing of the electronic states with vibrational levels, creating multiple new vibronic levels. Properties of the electronic state such as spin-orbit and orbital angular momentum are distributed into the new vibronic states which can reduce the apparent magnitude of these properties. This effect is increased for larger Jahn-Teller coupling. The Ham reduction of the orbital magnetic moment is $p = \exp[-1.974 \times (E_{JT}/\hbar\omega)^{0.761}]$, where $E_{JT}$ is the Jahn-Teller energy and $\omega$ is the vibrational frequency [149]. To get an estimate of the Ham reduction, an unquenched estimate of the $^1E$ orbital $g$–factor is required. Abtew et al [136] theoretically determined the dynamic Jahn-Teller energy in the $^3E$ to be $E_{JT}/\hbar\omega = 0.35$ with a vibrational frequency of $\hbar\omega = 71$ meV. Combining the experimentally measured orbital $l_{^3E}$ with the Jahn-Teller and Ham quenching factor $p_{^3E}$ gives the unquenched orbital $l'_{^3E}$ for the $^3E$ state (the unquenched parameters are denoted by a prime).

\[
p_{^3E} = \exp[-1.974 \times (E_{JT,^3E}/\hbar\omega)^{0.761}] \quad (9.24)
\]
\[
l'_{^3E} = l_{^3E}/p_{^3E}. \quad (9.25)
\]
CHAPTER 9. MAGNETIC CIRCULAR DICHR OISM OF THE NV CENTRE’S
FINE STRUCTURE

The singlet $^1E$ is expected to have an unquenched orbital $l_{^1E}$ twice that of the $^3E$
$l_{^3E}$ (i.e. $l_{^1E} = 2l_{^3E}$), which gives an expected Ham reduction of the singlet orbital
$l_{^1E}$ of,

$$p_{^1E} = \frac{l_{^1E}}{2l_{^3E}}$$

(9.26)

$$= 0.05 \leftrightarrow 0.025, \quad (l_{^3E} = 0.1 \leftrightarrow 0.2)$$

(9.27)

This reduction factor gives the $^1E$ Jahn-Teller energy ratio of,

$$\left(\frac{E_{JT}}{\hbar\omega}\right)_{^1E} = \left(\frac{\ln(p_{^1E})}{-1.974}\right)^\frac{1}{4\pi\alpha}$$

(9.28)

$$= 2.0 \leftrightarrow 2.3, \quad (l_{^3E} = 0.1 \leftrightarrow 0.2).$$

(9.29)

Abtew et al [136] determined that the triplet $^3E$ level has a Jahn-Teller energy ratio of $E_{JT}/\hbar\omega = 0.35$, as such the Jahn-Teller interaction found in the $^1E$ is approximately 6 times larger. As shown by Rogers et al [66] for the NV$^-$ IR ZPL and by Davies for the NV$^0$ ZPL [65], Jahn-Teller can explain the emergence of new $A_1$ emission level under uniaxial stress, this $A_1$ level was 115 cm$^{-1}$ above the ground $E$ vibronic level. As shown in figure 9.6, these extra levels appear when an $E$ electronic state interacts with $E$ vibrations producing vibronic states $E \otimes E = E \oplus A_1 \oplus A_2$. Using a relation from Ham [149], the energy of the $A_1$ and $A_2$ states above the ground $E$ state can be predicted using linear Jahn-Teller theory and the vibrational frequency, where the $A_1$ is $\Delta = \frac{\hbar \omega}{2} \left(\frac{E_{JT}}{\hbar\omega}\right)$ above the $E$ level. This linear relation assumes that the quadratic Jahn-Teller interaction is much smaller than the linear, but enough to break the degeneracy of the $A$ levels (i.e $\Delta \gg \delta$). Using the phonon energy from Abtew et al of $\hbar\omega = 71$ meV, the $^1E$ orbital $g$–factor value $l_{^1E} = 0.025$ determined from this MCD measurement and the $^3E$ orbital $g$–factor $l_{^3E} = 0.1$ value from Reddy et al gives a feature at $\Delta = 167$ cm$^{-1}$ (20.7 meV). Using the $l_{^3E} = 0.2$ from Hanzawa et al instead of Reddy et al gives a feature at at $\Delta = 127$ cm$^{-1}$ (15.7 meV). These values agree fairly well with the result from Rogers (115 cm$^{-1}$) et al and the characteristic energies by Robledo et al (16.6 meV) [83] and Acosta et al (15 meV) [64]. It is likely that the predicted values of the $A_1$ feature are slightly higher because of a non-negligible quadratic Jahn-Teller ($\delta$) which is not included in the above expression for $\Delta$. As such, it is expected that the measured $A_1$ level is the lower of the two $A$ levels. The values from Robledo et al, Acosta et al, Rogers et al and this work are from very different types of measurements that provide observations and quantitative agreement of a similar energy value. This is
further evidence of a strong Jahn-Teller in the $^1E$ and its likely role in the lower ISC.

Kehayias et al. [67] cite the presence of a dynamic Jahn-Teller effect in the $^1E$ to explain the disagreement of the absorption and emission bands of the IR ZPL. Using the Jahn-Teller energy measured here the vibronic levels and the strange phonon side-band disagreement of the singlet levels can be further investigated. This and other ab initio studies of the lower ISC can use this Jahn-Teller energy to try and un-pick the mysteries of the lower singlet levels. A strong Jahn-Teller interaction doesn’t easily explain why IR ZPL strain parameters are much larger than expected, so there are still remaining unanswered questions surrounding the NV$^-$ singlet levels but it is increasingly clear that strong vibronic effects are critical in the understanding of lower singlet level.

9.5.2 NV$^0$ zero-phonon line

Theoretical description

The NV$^0$ absorption is between an $^2E$ ground state and an $^2A_2$ excited state separated by a 575 nm ZPL. In this case the excited state has no orbital degeneracy but the ground state $^2E$ is split into two orbital branches with additional spin $-1/2$ branches. This can be described by the Hamiltonian,

$$H = g \mu_B \vec{S} \cdot \vec{B} + l \mu_B \vec{L} \cdot \vec{B} + \lambda \vec{L} \cdot \vec{S},$$

(9.30)

where $g$ is the spin $g$-factor and $l$ is the orbital $g$-factor, $\lambda$ is the spin-orbit interaction parameter and $z$ is along the NV axis. In the limit of a large magnetic field that splits the spin states much more than the orbital or spin-orbit terms, the secular approximation can be applied which transforms the spin coordinate system to be parallel to the applied field. Choosing $S_z \rightarrow S_z \cos \theta + S_x \sin \theta$. The orbitals remain fixed to the crystal so the orbital operator transforms as $L_z \rightarrow L_z \cos \theta$. The Hamiltonian can now be re-described as,

$$H = \mu_B g S_z B_z + \mu_B l L_z B_z \cos \theta + \lambda L_z (S_z \cos \theta + S_x \sin \theta),$$

(9.31)

where $S_z$ is now aligned parallel to the magnetic field direction. For these measurements the sample was aligned with a $\langle 100 \rangle$ face parallel to the magnetic field, as such $\cos \theta = 1/\sqrt{3} \Rightarrow \theta = 54.7^\circ$. Using Pauli matrices for both the orbital and spin operators the Hamiltonian can be written by the direct product $L \otimes S$ basis
Figure 9.7: Schematic of the NV$^0$ energy levels. Green and red arrows are the left and right circularly polarised absorption transitions, respectively. Absorption occurs between the $^2E$ ground state and $^2A_2$ excited state. Since the excited state is an orbital singlet, the only relevant optical selection rule is that spin is conserved. In the ground state, the zero-field splitting is due to spin-orbit $\lambda$ and the different gradients of the Zeeman splitting with respect to increasing magnetic field is due to the orbital $g$-factor.

which gives the eigenenergy solutions $E_{2E\uparrow\pm}$ where the $\uparrow, \downarrow$ signifies orbit and the $\pm$ signifies the upper or lower spin mixed branch.

$$
E_{2E\downarrow\pm} = -Bl\mu_B \cos \theta \pm \frac{1}{2} \sqrt{\lambda^2 + (Bg\mu_B)^2 - 2\lambda Bg\mu_B \cos \theta}
$$

$$
E_{2E\uparrow\pm} = Bl\mu_B \cos \theta \pm \frac{1}{2} \sqrt{\lambda^2 + (Bg\mu_B)^2 + 2\lambda Bg\mu_B \cos \theta}.
$$

(9.32)

These levels are shown in figure 9.7. The thermal population of the ground states also needs to be calculated when determining the difference between the left and right circularly polarised absorption. This is determined as $P_i = \exp \left(-E_i/k_BT\right)/Z$ where $Z = \sum_i \exp \left(-E_i/k_BT\right)$ is the partition function and $E_i$ signifies the different ground state energy levels. The thermal polarisation of the Zeeman split ground states becomes increasingly significant for lower temperatures and larger magnetic fields. The spin mixing in the ground state from spin-orbit does have an effect on the spin-conserving optical transitions to the excited state. However, this effect is limited to fields below $\lesssim 0.5$ T since at high fields the Zeeman contribution dominates over spin-orbit, as such it can be ignored for the magnetic fields used here.
Since the optical transitions are spin-conserving and the excited state $^2A_2$ is also expected to have a spin $-1/2$ Zeeman splitting, the effect of spin Zeeman is cancelled out between the states, and only the orbital Zeeman and spin-orbit components will be present in the optical transition energies. However, the effect of spin Zeeman is present in the thermal polarisation of the ground $^2E$ level and cannot be ignored. The excited $^2A_2$ level is assumed to be a simple spin $-1/2$ orbital singlet with the Hamiltonian $H = g \mu_B S_z B_z$ and eigenenergies $E_{^2A_2}^\pm = \pm \frac{1}{2} \mu_B g B_z$.

Performing moment analysis in a similar fashion to the IR transition, the first and zeroth MCD moments can be written respectively as

$$\langle \frac{Z_{L-R}}{E} \rangle_1 = \gamma \left[ - (\sigma_{\uparrow+} P_{\uparrow+} (E_{^2E\uparrow+} - E_{^2A+}) + \sigma_{\uparrow-} P_{\uparrow-} (E_{^2E\uparrow-} - E_{^2A-})) ight. \right.$$

$$\left. + (\sigma_{\downarrow+} P_{\downarrow+} (E_{^2E\downarrow+} - E_{^2A+}) + \sigma_{\downarrow-} P_{\downarrow-} (E_{^2E\downarrow-} - E_{^2A-})) \right]$$

(9.33)

$$\langle \frac{Z_{L-R}}{E} \rangle_0 = \gamma \left[ - (P_{\uparrow+} \sigma_{\uparrow+} + P_{\uparrow-} \sigma_{\uparrow-}) + (\sigma_{\downarrow+} P_{\downarrow+} + \sigma_{\downarrow-} P_{\downarrow-}) \right].$$

(9.34)

The zeroth absorption moment is similarly,

$$\langle \frac{Z_{L+R}}{E} \rangle_0 = \gamma [\sigma_{\uparrow+} P_{\uparrow+} + \sigma_{\uparrow-} P_{\uparrow-} + \sigma_{\downarrow+} P_{\downarrow+} + \sigma_{\downarrow-} P_{\downarrow-}] .$$

(9.35)

The resulting MCD moment ratios from the fitting parameters and moments are shown in figure 9.9.

**Results and analysis**

An example of the absorption and MCD spectra is shown in figure 9.8. As can be seen the sign of MCD signal flips with increasing temperature. This is due to the changing likelihood of absorbing a left or right circularly polarised photon as the ground state levels are thermally populated. As be seen figure 9.9, this flip occurs at approximately 5 K.

Using equations 9.15 to 9.18 the parameters from the curve fitting and the spectral moments can be compared. It can be seen from the error bars in figure 9.9 that moment analysis is inherently more accurate at determining the zeroth moment $\frac{A_1-A_2}{A_1+A_2}$ and vice-versa the curve fitting is more accurate at determining the first moment $d$. This makes sense as the moment method relies on amplitude to determine $d$ but this isn’t a problem for determining $\frac{A_1-A_2}{A_1+A_2}$. Similarly, the curve fitting requires width to determine $\frac{A_1-A_2}{A_1+A_2}$, but the first moment only needs to rely on amplitude. Although potentially more precise (smaller error-bars), the moment method is more prone to systematic inaccuracy than the fitting method as the fitting method uses a
Figure 9.8: (a) Example absorption ($Z_{L+R}/E$) spectra and (b) differential ($Z_{L-R}/E$) spectra for NV$^0$ ZPL with Gaussian fits at $B = 3$ T and $T = 1.46$ K and $B = 3$ T and $T = 20$ K (c-d). The linear background in the absorption spectra is due to nitrogen absorption. The non-zero offset of the MCD spectra is an experimental artefact and doesn’t affect the results, as a constant offset is added to the fitting model or the background is removed prior to moment analysis.
prior model that is more tolerant of faults or defects in the data. Moment analysis is essentially numerical integration, so any faults in the data will be included into the final result. These mentioned faults or errors are mostly just changes in absorption due to the bubbling of liquid helium or other similarly random changes in the optical path.

Although the moment analysis and curve fitting both agree relatively well, it isn’t immediately clear which method re-describes the physics more accurately. As such it was decided to compare the results for both independently when fitting the curves in figure 9.9 to the Hamiltonian. Substituting the probabilities and the energy values from the Hamiltonians into equations (9.33) and (9.34) gives analytical expressions for the first and second moments. These expressions were determined in Mathematica and are far too cumbersome to be conveniently written down or understood. However, they were parsed into Python for least-squares curve fitting as described in appendix B.3, the only free parameters were the orbital $g$–factor $l$ and the spin-orbit parameter $\lambda$ of the $^2E$ state.

In addition to the choice over using the moment or curve fitting data is the choice to fit with respect to temperature or magnetic field, and using the zeroth or first moments or both. It was decided not to pursue the extra effort of two-dimensional fitting of the temperature and magnetic field axes simultaneously because the results were self-consistent when fitting each axis independently. Every combination was fitted and all errors allowed to propagate through, the results of which are shown in table 9.1. It can be seen that there is strong consistencies amongst the resulting parameters for $\lambda$ and $l$. Taking a mean of all of the values in table 9.1 gives $\lambda = -10.5 \pm 0.2$ GHz and $l = 0.045 \pm 0.001$ and the resulting curves are plotted in figure 9.9. Some unrealistically small errors are shown in table 9.1 for some of the moment analysis rows. This is because in some spectra there is very small photo current noise and the lack of model to compare the expected result and determine an error from results in very high precision. For this reason, the errors shown in 9.1 weren’t used to compute a weighted average where the weights were determined from the error. The unrealistically small errors would dominate the weighted average.

It is not expected that there is a very large Jahn-Teller effect in the $^2E$ as the uniaxial stress and vibronic side band of the NV$^0$ are very similar to the NV$^-$ $^3E$ which shows a small Jahn-Teller effect. The quenching seen in the orbital $g$–factor found here doesn’t appear to equally effect the spin-orbit parameter which is in good agreement with the NV$^-$ $^3E$ spin-orbit parameter of 5.3 GHz. Note that the factor of two between the $^3E$ and $^2E$ spin-orbit parameters is expected because of the definition of the spin Hamiltonians and because $^2E$ has spin $S = 1/2$ and the
Figure 9.9: Fit of the first (a) and zeroth (a) MCD moments vs magnetic field and temperature (c-d). The dashed line is from the Hamiltonian using the mean fit parameters $\lambda = -10.5 \text{ GHz}$ and $l = 0.045$. The circle data points are obtained from curve fitting analysis, the star data points are from spectral moment analysis.
3\textit{E} is a spin \(S = 1\). The same analysis used for the singlet \(^1\text{E}\) result is now applied. The unquenched orbital \(g\)-factor should be equal to the NV\(^-\) \(^3\text{E}\) as both the \(^2\text{E}\) and \(^3\text{E}\) levels have a single \(e\) orbital. Comparing the observed orbital \(g\)-factors yields a Jahn-Teller reduction of \(p_{2E} = 0.18 \leftrightarrow 0.09\) using the same NV\(^-\) \(^3\text{E}\) orbital \(g\)-factors values of \(l = 0.1 \leftrightarrow 0.2\). These reduction factors give a Jahn-Teller energy of \(E_{JT}/\hbar \omega = 0.8 \leftrightarrow 1.3\), this is lower than the value determined by Davies [65] and calculated using \textit{ab initio} methods by Gali [214]. Using the vibrational frequencies from Abtey et al [136] and the linear Jahn-Teller expression presented by Ham [149], gives an expected \(A_1\) vibronic state above the \(E\) vibronic ground state with an energy separation of \(\Delta \sim 225\text{ cm}^{-1}\). This value does not agree with the experimentally determined \(~110\text{ cm}^{-1}\) measured by Davies [65]. This could be because a quadratic Jahn-Teller interaction plays a role in the NV\(^0\) \(^2\text{E}\) and splits the \(A_1\) and \(A_2\) away from where it was predicted by the previous linear expression. Or because we see the lower of the two \(A\) levels in the \(^1\text{E}\) uniaxial measurement and the higher of the two \(A\) levels in the \(^2\text{E}\) uniaxial measurement. In either case, it is clear that the quenching of the orbital \(g\)-factor is not the same for the \(^1\text{E}\) and \(^2\text{E}\) levels yet the uniaxial stress feature is at a very similar energy. Further evidence or reasoning is required to explain this disparity.

These results do not immediately explain why there hasn’t been observed fine-
structure in EPR or PLE measurements of NV\(^0\). Based on the spin-orbit parameter determined here and using a 9.6 GHz X-band EPR spectrometer, the NV\(^0\) \(2E\) EPR features are expected at \(B = \pm (\pm f - \lambda)/\mu_B g = \pm 0.032\) T, \(\pm 0.72\) T which are within the available field range of an EPR spectrometer. Similarly, a wideband tunable high-resolution laser should also be able to see these features in excitation spectroscopy (PLE) assuming sufficiently low strain.

There are three major reasons why EPR signals in the \(2E\) level have not been previously observed:

1. The orbital angular momentum is sufficiently quenched such that the level appears as a simple \(S = 1/2\) spin and its signal from ensemble EPR measurements is obscured by the signal from the much more abundant P1 centres. This quenching could occur because of a strong Jahn-Teller with local \(E\) modes causing a Ham reduction of the orbital angular momentum. A reduction in angular momentum could also be caused by fast orbital averaging over the orbital states by a weak Jahn-Teller coupling to a bath of acoustic \(E\) modes. This is seen in the NV\(^-\) \(3E\) at room temperatures [97, 215].

2. The lines are broadened beyond detection by a weak Jahn-Teller coupling to a bath of \(E\) acoustic modes. In the limit of coupling slower than spin-orbit the spin-resonances are broadened by phonon scattering with \(E\) vibrations.

3. Measurements have simply not been performed in the right parameter space or the signal was overlooked.

Given that we have observed a similar spin-orbit to the NV\(^-\) \(3E\) and the orbital \(g\)-factor is small but not negligible the first reason can be ruled out. That leaves the other two options as plausible. The results presented here will allow for a more targeted search of the NV\(^0\) fine structure using EPR or PLE.

### 9.6 Conclusion

These MCD measurements of the NV\(^-\) IR ZPL yield the first ever measurement of magnetic structure in the singlet states. The orbital \(g\)-factor of the singlet \(1E\) of 0.0284(4) is measured. This value is significantly reduced from the expected result based on measured \(3E\) orbital \(g\)-factor. Assuming the origin of the quenching is a dynamic Jahn-Teller distortion, a Jahn-Teller energy ratio \(E_{JT}/\hbar\omega\sim 2.2\) is determined. Using this energy, linear dynamic Jahn-Teller theory predicts that an \(A_1\) level from interactions with \(E\) phonons will occur at 147 cm\(^{-1}\) (18.2 meV). As shown in figure 9.6, a further quadratic Jahn-Teller splitting (\(\delta\)) is required to lift
9.6. CONCLUSION

the degeneracy of the $A_1$ and $A_2$ vibronic levels and this quadratic component is not represented by the previous linear expression. Given that expected discrepancy, the energy closely matches the uniaxial feature observed by Rogers et al [66] at 115 cm$^{-1}$ and the one-phonon characteristic energy in the decay model used by Acosta et al (15 meV [64] and Robledo et al (16.6 meV [83]). As such, these results offer further evidence that a strong Jahn-Teller interaction is present in the $^1E$ level and this is likely to have a significant role in the lower ISC.

The MCD measurements of the NV$^0$ ZPL are the first ever successful measurements of the fine structure of the NV$^0$ ground state. The results were successfully explained using a model with Hamiltonians that considers both the excited $^2A$ state and the ground $^2E$ state using spin $g$–factors of 2 and the parameters spin-orbit $\lambda$ and orbital $g$–factor $l$. It was found that there is a spin-orbit contribution of $\lambda = -10.5 \pm 0.2$ GHz and $l = 0.045 \pm 0.001$. The Jahn-Teller energy determined from the quenching of angular momentum doesn’t agree with the Jahn-Teller energy determined by Davies from the uniaxial stress feature, possibly due to quadratic Jahn-Teller effects. The possible reasons that the fine structure of the $^2E$ has not been previously observed are discussed. These results give a refined parameter space to perform further measurements of the NV$^0$ fine structure.
CHAPTER 10

Low temperature magnetic sensing of superconductors

10.1 Contributions

The experimental design and execution was performed by M.S.J. Barson, Z. Cheong and S. Thompson. The data analysis was performed by M.S.J. Barson.

10.2 Introduction

The knowledge of the thermal and mechanical properties of the NV centre are now known better than ever before. This knowledge enables the use of the NV centre to perform measurements in wide parameter space of extreme stress and temperatures; the conditions of many interesting experiments in material science. For example, exotic phase transitions in materials that occur at extreme conditions are often at pressures and temperatures that can be uniquely measured using the NV centre in diamond. The NV$^-$ spin is coherent for temperatures between mK and 600 K [31] and the tensile strength of diamond exceeds $\gtrsim 100$ GPa [194].

An ongoing area of research in material science is the study of materials that exhibit superconducting phases at very high pressures. For example, the highest temperature known superconductor, sulfur hydride at 203 K and 90 GPa [216]. To reach sufficient pressures in solid-state systems, these samples are often made by nanoindentation [217] or in a diamond anvil cell (DAC) [218]. As a result, the regions of interest are usually very small, such as individual particles or a compacted powder. The NV centre is particularly well suited to perform magnetometry on such small superconducting samples, due to its small sensor volume and magnetic sensitivity. Additionally, the NV$^-$ centre’s phase sensitive AC magnetometry abilities make it well suited to performing AC susceptibility measurements on superconducting
10.3. BASIC PROPERTIES OF SUPERCONDUCTORS

Supercconductors are defined by two qualities: (1) perfect conductivity and (2) perfect diamagnetism. A consequence of the latter is the Meissner effect, in which the magnetic field is expelled from the interior of a superconductor. This can be described by a magnetisation ($\vec{M}$) that opposes the applied magnetic field,

$$\vec{B} = \mu_0 (1 + \chi_m) \vec{H}$$  
(10.1)

$$\vec{M} = \chi_m \vec{H},$$  
(10.2)
CHAPTER 10. LOW TEMPERATURE MAGNETIC SENSING OF SUPERCONDUCTORS

Figure 10.1: B-T diagram for a type-II superconductor, the type-I region exhibits complete flux exclusion and perfect diamagnetism \( (\chi_m \to -1) \). The type-II region exhibits the vortex state, where partial flux exclusion occurs \( (-1 < \chi_m < 0) \). The dashed line, represents a low-field cooling down experiment like performed here, where \( T_{c2} \) is close to \( T_c \) and small bias magnetic field is applied.

\[ \chi_m \to -1 \]

where \( \chi_m \) is the magnetic susceptibility of the material. Below the critical temperature the magnetic field expulsion is complete for type-I superconductors \( (\chi_m \to -1) \). There is also a critical field \( (B_c) \) beyond which the superconducting state is destroyed and the field penetrates into the material again. Usually type-I superconductors have very low critical temperatures \( (T_c) \). Type-II conductors exhibit a second state, at magnetic fields above the critical field \( B_{c1} \), in which the magnetic flux is partially excluded from the sample and partially pinned to vortices \( (-1 < \chi_m < 0) \). Since part of the sample is superconducting the total resistance of the material is still zero despite having non-superconducting components. Above a second critical field \( (B_{c2}) \) the vortex state is destroyed, as such, the material becomes a normal conductor and exhibits magnetic field penetration. All high temperature superconductors are type-II superconductors generally with a very large \( B_{c2} \).

The critical magnetic fields shown in figure 10.1 have a quadratic temperature dependence which can be expressed as,

\[ B_{c1}(T) = B_{c1}(0) \left( 1 - \left( \frac{T}{T_c} \right)^2 \right) \]  

(10.3)

From figure 10.1 and equation 10.3 it is clear that it is desirable to perform measure-
ments of the critical temperature as close to zero magnetic field as possible, such that $B/B_{c2} \ll 1$ and $T_{c2} \approx T_c$.

The change in magnetisation is dependant on the applied field during cooling [223, 224]. If a type-II superconductor is in an applied field above its critical temperature, then the magnetic flux fully penetrates into the superconductor. If the material is then cooled and becomes superconducting, that magnetic flux is pinned into vortices within the superconductor. The flux from these vortices reduces the observed change in magnetisation during the phase transition. This process is referred to as field cooling (FC). Conversely, if no magnetic field penetrates into the sample when it becomes superconducting there is no flux pinning. When a field is introduced, the shielding diamagnetism [225] of the superconductor prevents magnetic flux entering the material. This case is referred to as zero-field cooling (ZFC), and it exhibits a larger change in magnetisation during a superconducting phase transition. Both of these processes are shown in figure 10.2.

Even for type-I superconductors which show no vortices, ZFC and FC can show a difference in sample magnetisation. If there are any defects in the material such as inclusions or holes that are non-superconducting, cooling in an applied field can trap magnetic fields in these inclusions. This occurs because shielding currents form around these inclusions when the remainder of the sample becomes superconducting. These shielding currents create a magnetic field which is aligned with the applied field and reduces the effective magnetisation of the sample. It is expected that this effect is exacerbated for granular or porous samples [226], as is likely to be the form of Ge-ST12 or similar high-pressure semiconductor based superconductors formed in a DAC.

Since the change in magnetisation for ZFC is much larger than FC; it is desirable to cool the sample down prior to applying any magnetic fields and performing magnetometry as the sample is warming up.

Conductivity measurements of superconductors can determine if any superconducting current paths are present within the material. This is essentially a measurement with the binary result of superconducting or not superconducting. Alternatively, measurements of the magnetic properties of the material can reveal more about the superconducting properties of a material. Measurements of the magnetic susceptibility and in particular the AC magnetic susceptibility can quantify the superconducting properties of a material. The pinning forces, superconducting grain fraction, grain size distribution and London penetration depth [222, 227] can be extracted using models and measurements of the complex AC magnetic susceptibility $\tilde{\chi} = \chi' + i\chi''$. Similar to complex refractive index $\tilde{n} = n + i\kappa$, where $n$ is the
refractive index and $\kappa$ describes the attenuation, the $\chi'$ and $\chi''$ components depend on the diamagnetism and magnetic losses of the superconductor, respectively. The values of $\chi'$ and $\chi''$ can be frequency dependent. However, the effect of changes in temperature on $\chi'$ and $\chi''$ are more commonly pursued. Due to the rich amount of information obtained from AC susceptometry measurements, this is the desired way to collect material information from superconductors. DC susceptibility is also a useful measurement due to its simplicity. DC susceptibility reveals details about the diamagnetic response of the sample, dependent on properties such as critical temperature, critical fields, sample geometry, anisotropy, hysteresis and other features not explicitly dependent on time.

As a proof of principle, measurements of the magnetic field, and therefore, the magnetic susceptibility of YBCO are investigated. YBCO is probably the most famous high temperature superconductor. It was the first superconductor discovered to have a critical temperature above liquid nitrogen temperature (77 K) [228]. First discovered by Wu et al in 1987, YBCO is a very well documented and understood type-II superconductor, the DC susceptibility of YBCO is shown in figure 10.3.
10.4. EXPERIMENTAL DETAILS

Figure 10.3: Measured DC susceptibility of YBCO as it undergoes a transition into the superconducting phase. Taken with permission from Wu et al [228]

10.4 Experimental details

A liquid helium cold finger continuous flow cryostat with a confocal microscope capable of imaging single NV centres was used (confocal system detailed in appendix A.2). The YBCO sample was glued to the coldfinger with a diamond \(\langle 100\rangle\) sample placed on top of the YBCO (figure 10.4) using a 3D printed sample holder. No glue was placed on the diamond to reduce unwanted fluorescence from the glue.

Single NV centres were implanted approximately 100 nm into one surface of a high-purity type-IIa diamond. A microwave waveguide was deposited directly onto the diamond surface nearest the NV centres using thermal evaporation (detailed in appendix A.3.1). The NV/waveguide side of the diamond was placed down against the superconductor and this was the side imaged with the confocal through the diamond. An external field was applied perpendicular to the surface of the YBCO using a ring of magnets in a 3D printed holder or solenoid placed around the objective lens. The temperature of the cold finger was monitored using temperature sensing diodes (LakeShore DT670) and the temperature was held constant using a nichrome resistive heater and PID control (LakeShore 331). The diamond face is at least 50 \(\mu\)m from surface of the YBCO, due to the microwave waveguide contacts at the interface between the diamond and YBCO. In future experiments this distance will be reduced, allowing for the possibility of mapping the effect of individual superconducting vortices. Although the flux pinning occurs to localised sites that are
Figure 10.4: Placement of YBCO and diamond on cold finger. A 3D-printed structure (not shown) was used to push the diamond onto the YBCO without needing glue near the YBCO-diamond interface. The microwave wire and waveguide is at the YBCO-diamond interface, the microwave circuit was integrated into the cold finger, as such only one conductor connects to the diamond. The YBCO was glued to the cold finger.
\[ \sim 200 \text{ nm in size and spatially distributed throughout the YBCO [229]}, \] the NV\(^-\) centres in the measurements presented here are far enough from the YBCO surface to only see a mean magnetic field from a localised area. The YBCO is much larger than the area surrounding the NV\(^-\) centre, as such the YBCO can be approximated as a semi-infinite slab.

10.5 Results and analysis

10.5.1 ODMR magnetometry

The NV\(^-\) spin-resonance frequencies due to an applied magnetic field are [230],

\[
f_{\pm} = D + \frac{3\gamma_e^2 B_\perp^2}{2D} \pm \gamma_e B_\parallel \sqrt{1 + \frac{\gamma_e^2 B_\perp^2}{4D^2 B_\parallel^2}},
\]

where \( \gamma_e \) is the NV\(^-\) gyromagnetic ratio, \( B_\parallel = B \cos \theta \) and \( B_\perp = B \sin \theta \) and \( \theta \) is the angle between the field direction and the NV axis. When the transverse and parallel field components are approximately equal (\( B_\parallel \sim B_\perp \)) and the Zeeman interaction is much smaller than the zero-field splitting (\( \gamma_e^2 B_\perp^2 \ll D \)) then the difference in frequency of the two spin branches is,

\[
\Delta f = f_+ - f_- \approx 2 \gamma_e B_\parallel.
\]

Similarly, the average frequency of the two spin branches is,

\[
\bar{f} = \frac{f_+ + f_-}{2} = D + \frac{3\gamma_e^2 B_\perp^2}{2D}.
\]

As such, the difference in frequency (\( \Delta f \)) is dependent on axial magnetic field \( B_\parallel \) only. The average frequency (\( \bar{f} \)) is quadratically dependent on transverse magnetic field \( B_\perp \) and to any changes in \( D \), most likely due to temperature fluctuations.

10.5.2 Comparison with previous results

Performing DC CW ODMR on the NV\(^-\) centres close to the YBCO/diamond interface enables the effects on the magnetic field due to the YBCO to be monitored by observing the spin-resonance frequencies. For this measurement the YBCO was cooled down (FC) in a 134 G field perpendicular to the YBCO and \( \langle 100 \rangle \) diamond face, this gives a 77.5 G magnetic field projected along the NV\(^-\) axis. A drop in
magnetic field occurred at approximately 77 K as shown in figure 10.5(a). Using the temperature dependence of the DC magnetic susceptibility from Wu et al [228], the measured field can be see to be in good agreement with the expected YBCO magnetic behaviour. The vertical axis of Wu et al’s susceptibility was scaled to match the field measured here, but still clearly shows the correct temperature dependence as the temperature axis was not scaled. The rescaling of the magnetic field is justified as the measured magnetic field is dependent on many experimental factors such as sample volume, geometry, NV-superconductor distance and applied magnetic fields during cooling [224]. These unknown factors are all in principle easily determined, however this was not pursued for these proof of principle measurements.

10.5.3 Effect of applied field during cooling

The effect of different applied magnetic fields during cooling can be seen in figure 10.6(a). For the zero-field cooling (ZFC) measurements, no magnetic field (remnant field < 4G) was applied until the YBCO sample was cooled to approximately 40K. A magnetic field of approximately 51 G was applied and the samples warmed up. For the FC measurements a field of approximately 135 G was applied at room tem-
10.5. RESULTS AND ANALYSIS

Figure 10.6: Difference of change in magnetisation of YBCO cooling down in an applied field and cooling down (FC) in zero applied field (ZFC).

perature and then the sample was cooled down. The ZFC case shows a magnetic field reduction of $\sim 50\%$ and the FC case shows a magnetic field reduction of only $\sim 7\%$. This agrees with the expected behaviour and highlights the benefit of cooling the sample prior to performing any magnetometry with an applied field. It is expected that the magnetic field did not go completely to zero due to the relatively large YBCO-NV distance.

10.5.4 Measurement of critical temperature

The phenomenological model used to describe the magnetic field during the superconducting phase transitions is,

$$B(T) = \frac{B_0 - B_Q}{2} \tanh \left( r (T - T') \right) + \frac{B_0 + B_Q}{2},$$  \hspace{1cm} (10.7)

where $B_0$ is the applied bias magnetic field, $B_Q$ is the reduced magnetic field at low temperature, $r$ is a parameter describing the steepness of the magnetic field change through the phase change and $T'$ is a variable that locates the position of the phase change on the $T$ axis. This model was chosen as the resulting behaviour showed a trend similar to a tanh function. The physics describing the curve showing change in magnetisation across the phase change is complicated [231] and often determined numerically [224], which is beyond the scope of this chapter. The resulting fits to this model are shown in figure 10.7. Using a cut-off $c$ to determine the critical
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Choosing a cut-off of $c = 0.99$ when the magnetic field starts to reduce yields critical temperatures of $T_c = 89(1)$ K and $83(5)$ K for the ZFC and FC measurements, respectively. These values are both slightly colder than the accepted value of 93 K [228], probably due to a small heat loss between the temperature sensing diode and the sample. In which case the sample is actually warmer than what the temperature sensor is indicating it should be. This could be due to the microwave coaxial cable conducting extra heat to the cold finger, but not well thermally connected to the area of the temperature sensing diode. Future designs can easily thermally anchor the microwave coax more sufficiently. Additionally, this particular YBCO sample was accidentally cleaned with some “pirhana” acid mixture which caused some damage to the surface of the YBCO.

To rectify the temperature measurement ambiguity, ODMR thermometry measurements can be performed separately to the magnetometry measurements. The thermometry can be used to calibrate any heat losses or temperature differences not reflected in the value from the temperature sensing diode. Performing thermometry and magnetometry during a sharp change in magnetic field due to the superconducting phase transition is more challenging than static magnetic field ODMR thermometry. This is because the transverse field is also quadratically affecting the mean spin resonance frequency ($\bar{f}$) as shown in figure 10.7. However, the axial field component can be measured separately and the NV orientation relative to the magnetic field is well known. Using this information, the transverse component of the magnetic field can be predicted from the axial projection. The effect of $B_\perp$ can then be subtracted from $\bar{f}$ to extract only the temperature shift of $D$. Demonstrating this principle, the curves in figure 10.7(b) take the transverse projection of the magnetic field measured in figure 10.7(a) with the temperature dependent $D$ shift included. The results shown here have a large amount of noise resulting from the non-optimal experimental conditions. Since this was the very first proof of principle measurement little experimental optimisation occurred. Despite this noise, it is clear that the transverse projection of the magnetic field and the measured temperature shift are reflected by the measurement. Using lower power microwaves to limit power broadening and pulsed measurements that offer better sensitivity will enable for an accurate thermometry calibration that is performed concurrently to axial magnetometry. Alternatively, a $\langle 111 \rangle$ orientated diamond can be used to limit the

\[ \tanh (r (T - T')) = c. \quad (10.8) \]
transverse component of the magnetic field and its affect on $\tilde{f}$, resulting in simpler determination of the temperature from the $D$ shift.
Figure 10.7: (a) The component of the magnetic field along the NV axis determined from the difference in frequencies $\Delta f$. The fit is to the phenomenological model shown in equation (10.7). The purple and blue data are from zero-field cooling (ZFC) and field cooling (FC) respectively. The shaded areas represent the critical temperature $T_{c1}$ based on a 99% cut-off within $1\sigma$. (b) The average frequency using the magnetic field from the fit in (a) with the thermal $\Delta D(T)$ dependence included, as shown in equation (10.6). This plot only shows the fitting used in figure (a).
10.6 Outlook

The total magnetisation developed by the superconductor opposing the applied magnetic field is heavily sample geometry dependent [232]. As such, the exact volume or mass of the material must be known to absolutely quantify its magnetic susceptibility $\chi_m$. Since the NV centre can perform magnetometry measurements at nanoscale dimensions, the requirements of the sample geometry are less stringent. For example, a macroscopic piece of YBCO appears as a semi-infinite slab to an NV centre near the surface. Similarly, the spherical nanoparticles expected in a powder of superconducting material can be approximated as point like magnetic dipoles. These geometric simplifications reduce the challenge of determining the intrinsic material properties from the observed susceptibility.

Due to the NV$^-$ centre's phase sensitive AC magnetometry abilities of very weak fields at the nanoscale, there is exciting scope to employ NV$^-$ centres to perform susceptometry in superconducting material science. It will be possible to measure the complex susceptibility for superconducting samples that are too small for conventional bulk susceptometers. The in and out of phase components of the superconductors magnetic response can easily be measured in a similar manner to the in and out of phase mechanical response detailed in section 6.4. The NV$^-$ centre offers the high magnetic field sensitivity needed to perform susceptibility measurements at very small magnetic fields. As shown in figure 10.1, this is needed to measure phase changes close to the critical temperature [222]. The NV$^-$ centre's magnetometry performance over a wide temperature range is important as many high-temperature superconductors of interest have critical temperatures too high for other superconducting micro-susceptometer devices such as SQUID magnetometers [233]. Although, some bulk SQUID susceptometers have a separated sample space so the sample can be warmer than the SQUID magnetometer, however this design cannot easily be used for imaging or sensing of very small samples.

To be as close as possible to the zero-field critical temperature ($T_c$), it is beneficial to perform the susceptibility measurements at a magnetic field strength as low as possible. However, most sensitive AC magnetometry measurements using NV$^-$ centres apply a relatively large DC bias magnetic field ($\gtrsim 100$ G) to obtain well separated spin resonances. This is beneficial because well separated spin resonances allow for faster Rabi frequencies (up to detuning/separation of the other spin branch). This can give faster spin-control pulses, which increases the range of the NV$^-$ magnetometry sensitivity frequency band. Additionally, a DC bias field shifts the Larmor precession frequency of the unwanted $^{13}$C nuclear spin bath out...
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of the useful magnetometry sensing band. The gyromagnetic ratio of the $^{13}$C nucleus is 10.7 MHz/T \cite{93}, so to shift the Larmor frequency of the $^{13}$C spin bath out of the sensing band ($f > 1/T_2$) for a NV$^-$ with $T_2 \approx 10 \mu$s requires an applied DC field of $B \gtrsim 100$ G. As such, performing AC susceptometry using NV$^-$ centres with a very small bias field will require slow Rabi frequencies with long and weak microwave pulses. This will require good quality NV$^-$ centres with long coherence times for optimal sensitivity. It will also be required to perform the magnetometry at a frequency where the effect of the $^{13}$C Larmor precession is minimised, that is, at the peak of a $^{13}$C ‘revival’ \cite{54}.

An alternative magnetometry technique is to use the Rabi frequency (as opposed to the previously described Larmor frequency) of the NV$^-$ spin \cite{234}. This is advantageous as there is no need to apply a DC magnetic field. The effect of the superconductivity of the sample can be measured using the 2.87 GHz microwave field and the resulting Rabi frequency. Superconductors are routinely used for GHz frequency resonators and are not fundamentally limited to any particular frequency band. The Rabi frequency $\Omega = \sqrt{\delta^2 + (\vec{\mu}_{NV} \cdot \vec{B})^2}/\hbar$ for zero or constant detuning $\delta$ is dependent on the magnetic field strength $B$ only. Changes in temperature can shift the zero-field spin resonance frequency ($D$). This will introduce an undesired detuning that will effect the observed Rabi frequency. As such, to correct for the temperature shift in $D$, a refocussing of the applied microwave frequency should be applied at each temperature. This will ensure that any changes in Rabi frequency are due to changes in $B$ only. Unfortunately, it is not possible to measure the out of phase component of the microwave field since there is no external phase control of the NV$^-$ spin and the superconducting behaviour cannot be switched off. As such, these two methods offer complementary information. The Rabi method can measure very weak field information at 2.87 GHz such as the critical temperature, where as the Larmor method can use a larger bias field and measure the complex AC susceptibility and associated material properties and superconductor quality.

10.6.1 Cryo-NV-DAC

A natural conclusion of studying materials that have interesting magnetic properties at high pressures using a DAC is to integrate NV$^-$ centres into the diamond anvils. Using the information acquired in this thesis, such a device could perform unprecedented nanoscale sensing of exotic phase transitions across a magnetic-temperature-pressure parameter space not available to other devices.

Magnetometry on the sample can be performed and the effect of mechanical and
10.6. OUTLOOK

thermal shifts of the NV$^-$ centre factored out from the result. Pressure measurements can be performed using the NV$^-$, removing the requirement for a ruby sample or similar pressure sensor. Similarly, temperature measurements can be performed with the NV$^-$ centre. This will be useful as the NV$^-$ within the diamond anvil will be very close to the sample, giving a more accurate measurement of the sample’s temperature than a convention temperature sensor which would be further away and could suffer from thermal contact losses.

High purity diamond anvils exhibiting low fluorescence intended for Raman spectroscopy are commercially available. NV centres could be created at the high pressure surface of these diamond anvils either by nitrogen implantation or by delta-doping and CVD overgrowth. These methods would create NV centres with a depth sufficient for magnetometry. Simple calculations of the estimated required sensitivity for susceptometry measurements have specified that the NV centres can be up to 40 $\mu$m away from our sample. As such, shallow NVs are not a strict requirement for these measurements.

A drawing of such a device is shown in figure 10.8. The DAC could be placed at the end of a sample rod that is suspended in a liquid helium bucket cryostat. The temperature could be controlled by adjusting the helium flow valve and by using a heater. Temperature sensing diodes could also be used to monitor temperature. Microwaves could be delivered to the NV using a loop or two-wire transmission line around the diamond anvil containing the NV centre. It could be possible to adjust the DAC pressure screws from outside the cryostat using a long rotating rod.

The optics could be free-space coupled down the bore of the sample rod. For confocal imaging, either the DAC or the objective could be scanned using a cryogenic scanning stage. Alternatively, tube lenses down the bore of the sample rod could allow for galvos to scan the beam angle into the objective lens. An objective lens that has a sufficient working distance to image through the diamond anvils (up to $\sim$3 mm) at cryogenic temperature with minimal aberration would be required. This is likely to be one of the biggest challenges for such a device. If single NV$^-$ centres cannot be imaged due to these limitations, the system could still perform magnetometry on small ensembles of NV$^-$ centres with sufficient sensitivity and spatial resolution for many interesting superconducting magnetometry measurements.
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10.7 Conclusion

The phase change of superconducting YBCO has been determined using NV based magnetometry. This result agrees well with previous measurements of the susceptibility of YBCO and displays the effects of cooling at different magnetic fields. This method can now be extended to new superconducting materials in particular microscopic materials that are difficult to measure using conventional techniques. AC magnetic susceptometry is discussed as the desired method to determine the magnetic properties of superconducting materials. Ultimately, an ideal and versatile device would consist of NV centres integrated into a diamond anvil cell (DAC). Such a device (Cryo-NV-DAC) is described. Its combined thermometry, magnetometry and piezometry capabilities represents a culmination of much of the work presented in this thesis and could provide an invaluable tool in the study of high-pressure materials.

Figure 10.8: Drawing of a cryo-NV-DAC device
Conclusion

The aim of this thesis was to investigate the mechanical and thermal interactions of the NV centre to improve the fundamental understanding of the NV centre’s properties and its potential applications. Greater understanding of the fundamental behaviour of the NV centre’s mechanical and thermal properties can enable new metrology capabilities. This adds to the NV centre’s already impressive metrology abilities, allowing for novel hybrid sensors that can measure an unprecedented number of phenomena with a single device at the nanoscale. Improved fundamental understanding of these phenomena will also allow for better outcomes in quantum information applications of the NV centre. As their effects can now be designed to be enhanced or restricted, improving device capabilities and utility.

The NV<sup>-</sup> centre’s fundamental spin-mechanical behaviour was described. Until now the scientific community had failed to adequately describe the NV<sup>-</sup> centre’s spin-mechanical behaviour in a repeatable and complete fashion. This thesis extends ideas initially used to describe the mechanical behaviour of optical transitions to also describe the ground state spin resonance. Since the stress or strain of a solid body can only be represented by a tensor, this method uses the power of group theory to fully incorporate the full stress tensor into the spin-mechanical description. This model was characterised using uniaxial stress measurements and the extracted parameters detailed. By using this complete model, the measured parameters not only agree with, but can also unify the incompatible observations in the literature.

By constructing mechanical structures such as cantilevers or pillars, force measurements utilising the spin-mechanical interaction can be implemented. Such measurements were demonstrated using a diamond cantilever. There was complete agreement between the force measured from classical bending mechanics and the force measured from the spin-mechanical shift of the NV<sup>-</sup> spin resonance. This validates our spin-mechanical characterisation and the application of bending me-
The resulting sensitivity of such NV spin-mechanical force sensors is well placed with other similar technologies ($\sim 100\text{pN}/\sqrt{\text{Hz}}$). By taking advantage of the NV centres uniquely small size, high density force sensors such as nanopillar arrays were envisioned. These devices could measure a spatial map of forces at a resolution and sensitivity not yet realised in other technologies. Such force mapping devices could have significant implications for biological force sensing and imaging. By taking advantage of the NV centres ability to perform frequency and phase sensitive AC measurements, resonant mechanical mass sensors were described. These devices can perform mass sensing of an adsorbate mass at equal or better sensitivity than similar resonant mechanical mass sensors ($\sim \text{zm}/\sqrt{\text{Hz}}$). By utilising the NV centres small size, multiple NV centres can be integrated into a single mass sensor and by performing phase sensitive measurements the mass distribution of an adsorbate can be imaged. This ability is unique to NV spin-mechanical mass sensors. Such devices can also perform all of the other metrology abilities of the NV centre. For example, both the structural (mass sensing) and chemical (NMR) information could be extracted from an adsorbate using a single device.

The fundamental behaviour of the NV$^-$ centre’s optical and spin resonances due to changes in temperature was described and characterised. This method extended theories that had previously been successfully used to describe the temperature behaviour of the NV$^-$ and NV$^0$ optical resonances. Prior to this work describing the origin of thermal behaviour of the NV$^-$ spin-resonance was an outstanding problem. Multiple efforts had previously tried to use the thermal expansion of diamond to describe the observed behaviour without success. The explanation employed in this thesis includes a quadratic electron-phonon interaction that combines with the thermal expansion to describe the observed resonance shift. It is found that the quadratic electron-phonon process dominates over the thermal expansion component. This is beneficial for thermometry as replicatable measurements can be made between diamonds that have significantly different thermal expansion due to impurities. This removes the overhead of calibrating each temperature sensor, an insurmountable challenge if utilising nanodiamonds for thermometry.

The NV$^-$ hyperfine interaction with first shell $^{13}\text{C}$ nucleus was investigated as a function of temperature. This measurement atomiscopically probed the NV$^-$ electronic orbitals as the diamond deforms due to the thermal expansion. It was found that the hyperfine interaction does not change across a very large temperature range. This rules out any net changes in the spin density at the location of a first shell $^{13}\text{C}$ as the diamond expands. It also rules out any change in orbital hybridisation or reorientation. Given these results, the electron orbitals must simply...
follow the carbon nuclei as the diamond expands or contracts. This is the first atomscopic measurements of the NV$^-$ electrons behaviour due to the deformation of the surrounding diamond.

Two of the most prominent unsolved mysteries of the NV centre were investigated. One such mystery was the behaviour of the NV$^-$ singlet levels and their role in the critical spin-polarisation and spin-readout abilities of the NV$^-$ centre. The other investigated mystery was determining the fine-structure of NV$^0$ and why it had previously been undetected. Magnetic circular dichroism (MCD) measurements performed the first ever observations of any magnetic structure in the NV$^-$ singlet levels. A large quenching of the orbital angular momentum was discovered, providing further evidence that a significant Jahn-Teller interaction is present in the $^1E$ level. The Jahn-Teller energy of this interaction is in agreement with previously determined Jahn-Teller measurements and also matches the characteristic energy describing the decay of the lower ISC. Suggesting that a significant Jahn-Teller interaction is responsible for the behaviour of the lower ISC. These results will aid in further investigations of the lower ISC, including ab initio studies of the role of vibrational coupling in the lower ISC. The magnetic fine structure of the NV$^0$ was also observed using MCD measurements. This is the first time any fine structure of the NV$^0$ $^2E$ or $^2A_2$ states has been observed. The spin-orbit parameter and orbital $g$-factor of the ground $^2E$ level were measured. These observations rule out some possible reasons for the absence of observations of the NV$^0$ fine structure. Future investigations can re-examine EPR spectra in the parameter space outlined by these measurements and investigate whether phonon induced broadening is responsible for the absence of observed signals.

New abilities in multi-mode sensing performed over a wide range of temperatures and pressures are now possible thanks to new understanding of the mechanical and thermal properties of the NV centre. Since the NV$^-$ spin is coherent from mK to 600 K and the mechanical properties of diamond are extreme, significant metrology advances in material science at extreme conditions can be envisioned using the NV centre. The magnetometry abilities of the NV centre for the measurement of superconducting phase transitions in high pressure materials are demonstrated and discussed. The design for a new multi-purpose device with NV centres integrated into a diamond anvil cell is proposed, the Cryo-NV-DAC. The magnetic-temperature-pressure sensing ability of this device represents a culmination of much of the work presented in this thesis and could provide an invaluable tool in the study of nanoscale high-pressure materials.
APPENDIX A

Experimental details

A.1 Uniaxial stress press

The uniaxial measurements were probably the most frustrating experiments to perform during this work. The fracturing of a diamond is fast, often unexpected, expensive and irreversible. Hopefully this section will provide the necessary details to recreate these experiments and avoid the pitfalls that I found.

Although diamond is the hardest (resistance to deformation) known bulk material it has relatively unimpressive toughness. Toughness is the ability of a material to absorb energy and plastically deform before fracture. Diamond also has certain crystal plane directions which are weaker than other crystal directions, this is exploited by the gemcutters who shape diamonds by cleaving along these planes. By far the weakest plane is parallel to the $\langle 111 \rangle$ direction [194, 235]. These $\langle 111 \rangle$ planes form an octahedral set of weak crystal plains within the cubic structure. Great care must be taken to ensure that the opposing faces of the uniaxial press are very flat and very parallel to the face of the diamond to avoid any non-uniaxial stress to develop which could be along one of the weaker cleavage planes. When fracture does occur in these measurements it is evident from observing the fractured faces occurs parallel to $\langle 111 \rangle$.

Since diamond is the hardest known material, the anvil face will yield before the diamond will. This results in a deformation of the anvil surface, which destroys the flatness required for safe operation. To limit this process, the anvil surface should be as hard as possible. Sapphire was trialled as an anvil surface, but suffered from the similar poor toughness of diamond, i.e. unpredictable catastrophic failure. Sapphire was desirable due to its non-conducting and non-magnetic properties. Flame-hardened tool steel was ultimately chosen as it can be easily machined and
then hardened. Also, if the deformation of the steel anvil face is considerable, the
damaged hardened faces can be annealed, machined flat, re-hardened and then re-
used. Unfortunately the ferromagnetic properties of the steel resulted in unwanted
magnetic fields at the sample. Since the Zeeman shift of the NV\(^{-}\) spin levels is so
large, these field had to be nulled by an externally applied magnetic field.

Force was applied to the anvils in the press using a pneumatic piston actuator
and a gas bottle with a low pressure regulator. The gas pressure was measured
using a simple mechanical gauge. This force could be applied using other techniques
such as weights or hydraulic methods. It would be recommended to add a high force
load cell directly above the sample anvils, reducing any uncertainty in characterising
piston area and force response.

Ideally, the uniaxial press should be able to operate within a cryostat as to
simultaneously resolve the optical shifts and the perform ODMR measurements.
However, most liquid He cryostats require a very long (1.5 m) sample holding rod
to isolate the cold end from the room temperature end attached to the cryostat.
Additionally, this rod should be made out of thin and non-thermally conductive
material to prevent excessive liquid He boil off. This long length and requirement
of minimal material bulk present a trade off in trying to make a uniaxial press that
will not buckle under compressive loading. Carbon fibre rods and tubes were trialled
for our press, but they fractured unpredictably, were difficult to machine to suitable
tolerances and were difficult to join together. Stainless steel rod and tube presses
were used, but stainless steel often has considerable internal strain and is prone to
warping. As such, the long compressive loading on the central rod sometimes led to
slight buckling and slight non-uniaxial loading of the sample - resulting in diamond
fracture.

To prevent this possible non-uniaxial loading of the crystal, one of the anvils
was designed to be a half ball-cone structure. This was achieved by grinding a ball
bearing to an approximate hemisphere, this ground flat face formed one side of our
press. The round side of the ball was lubricated, placed into a cone and was free to
pivot preventing any resultant torque at the sample.

To maintain parallel placement of the diamond against the anvil, a 3D printed
mask the exact thickness of the diamond was designed (see figure 4.2(a)). The mask
had an outer diameter that was matched to the bore of the press and an aperture
to hold the diamond exactly in the centre of the press. This flat mask helped to
align the diamond and half ball-cone to be as parallel and as central to the faces of
the press as possible. The upper anvil was long and fitted tightly into the bore of
the press ensuring that it was axially aligned to the sides of the press with its face
parallel to the diamond surface. Small paper gaskets were then added between the diamond and the anvils. These paper gaskets would hopefully deform into any small roughened features on the anvil faces and present a flat as possible anvil face to the diamond. The 3D printed mask also had channels for the microwave transmission wires and an optical aperture for the laser excitation and measured fluorescence. Once all of the pieces were assembled in the press and the anvils were in contact and parallel to the faces of the diamond, a few kilograms of force was manually pushed on the press to seat everything into place. Once this was satisfactorily demonstrated, the piston was connected and a very small amount of pressure set on the gas regulator (< 3 psi → 7 MPa at diamond). A vent valve (figure A.1(c)) on the gas line was very slowly closed and the piston allowed to build pressure. If the diamond was not appropriately aligned with the face of the anvil it would of broken by this point. If everything is appropriately seated, then the pressure can be slowly increased to maximum pressure. This processes of the seating the diamond with the 3D printed mask, paper gaskets and half ball-cone produced the most repeatable measurements and least unwanted diamond fractures.
Figure A.1: (a) Photograph of press used for room temperature uniaxial stress ODMR measurements. Copper coax is for microwave delivery, and apertures for optical access. (b) Half ball-cone insert used as lower anvil of the press. (c) Gas line plumbing, all made with 1/4" pneumatic tubing and push-in fittings. A low pressure regulator is needed to adjust the pressure after the bottle, many common gas regulators are built for high pressure. This experiment only needed pressures up to 2 MPa but the bottle is filled up to 15 MPa. The gauge monitors the line pressure. A three way valve is used to engage and release the gas pressure onto the piston. A flow gauge is useful to diagnose leaks and determine if the valve is slightly open.
A.2 Confocal microscope

Although confocal microscopy for the use in NV experiments is a very well established and utilised technique, there were no working confocal microscopes in my group before I joined. This appendix should hopefully serve as a handbook to constructing a confocal microscope as the procedure can be difficult for the uninitiated, as I found it to be.

The benefits of imaging single NV centres over ensembles are reduced inhomogeneous broadening, larger optical spin contrast and nano-scale spatial resolution. To image single NV centres a very high resolution microscope is required. The reasons for this are numerous. The greater the resolution the easier it is to distinguish single NV centres that may be close to each other; more photons from a single NV can be collected giving larger signals; And the greater the resolution the tighter the confocal volume and the larger background rejection.

A confocal microscope contains two pinholes in the optical path, one on the excitation path and one on the detection path. For the microscopes used during this thesis, the first pinhole on the excitation path consisted of the exit core of a single mode fibre (Fibercore SM450 fibre $\sim 3\mu m$) that the laser was coupled into. The second was a free space pinhole ($\sim 25\mu m$) which was placed before photon detector or the core of a fibre if the the photon detector is fibre coupled. The combined effect of these two pinholes is that detected light must come from a very confined volume within the sample. In practice these two pinholes must be carefully aligned so that the effect of the excitation and detection volumes overlap and all out of focus or unwanted light is rejected and the maximum desired excitation intensity is collected. These types of microscopes can achieve the highest possible resolution using conventional optics - so called diffraction limited systems.

A major component of the microscope is the objective lens. This lens is named “objective” because it is the lens that is closest to the object or sample. The most important metric of the performance of this lens is its numerical aperture (NA). This quantity defines the solid angle of light that can captured by the lens. This single quantity is more important than the magnification or focal length regarding imaging quality and achievable resolution. The numerical aperture is defined as $NA = n \sin \theta$, where $n$ is the refractive index of the medium between the lens and the measured object and $\theta$ is the maximum angle of an accepted cone of light from the object. The diffraction limit is given as $\lambda/2NA$, since the wavelength the excitation and emission light is essentially fixed the only improvable figure is the NA of the lens.
Figure A.2: Schematic of confocal microscope with cold finger cryostat. Acronyms are: PBS - polarising beam splitter, AOM - acousto-optic modulator, QWP - quarter wave plate, APD - avalanche photodiode, DAQ - digital acquisition board.
For an objective working in air \((n \approx 1.0)\) the highest achievable NA in practice is \(\sim 0.95\), limiting the resolution of the system to \(\sim 270\) nm. However, for NV centres which are already identified as atomic-sized single photon emitters the resolution is not important as long as the NV centres are many diffraction limited widths apart from each other and can be uniquely identified. However, NA is much more important to the collection efficiency, as shown in Figure A.3. The higher the NA, the more photons that are collected per unit time and the higher the sensitivity of our measurement. The optical lifetime of the excited state is 12 ns, with an emission rate of 83 MHz. However, the emission photon count rate from an NV within a bulk piece of diamond is usually about 0.3 MHz. More emission can be achieved from nanodiamonds or NV centres within photonic structures such as nanopillars due to better directional output of the emitted light. To maximise the effective NA of the objective lens, a beam which is as collimated as possible should be passed in to the rear aperture of the objective lens. The entire size of that aperture should be filled with the light of the beam. The beam from the laser should be expanded to be larger than the entrance aperture of the objective. To achieve maximum resolution a beam of a Gaussian intensity profile should be used which will result in a Gaussian ellipsoid confocal volume \(I = I_0 e^{-2x^2/\rho_0^2} e^{-2y^2/\rho_0^2} e^{-2z^2/z_0^2}, z_0 = \frac{1.5\lambda}{NA^2}\) and \(\rho_0 = \frac{0.44\lambda}{NA}\). Since the laser is usually coupled out of a single mode fibre, this Gaussian profile is easily achieved.

The photon detection rate must be high compared to the dark count rate of our detectors. The confocal microscopes built for this work used either an MPD or Perkin-Elmer single photon avalanche photodetector (APD), these detectors have a dark count of approximately 100s Hz, which is appreciably low given the emission from a single NV with a high NA (1.4 oil immersion) is \(\sim 300\) kHz. In practice the background is not limited by the dark counts of the detector but usually from scattered light reaching the detector.

To map the position of NV centres the confocal volume of the microscope must be scanned spatially within the sample. This can be achieved by moving the relative position of sample or the objective using a piezo-nanopositioning scanner. It can also be achieved by scanning the angle of the beam entering the objective by use of scanning mirrors (galvonometer or galvos). Since galvos only give a scan in XY, movement in the Z axis must be provided by scanning the sample or the objective relative to each other with a piezo-actuator. To generate a change in angle of the full range of the galvos a 4f optical system is used to refocus the light along the central axis and remap the angle from the galvo into an angle at the lens as shown in Figure A.4(a). The angle and diameter of a beam out of the 4f system are related the focal
Figure A.3: Collection efficiency for various NA objectives, calculated for an oil immersion lens with refractive index of $n = 1.5$. This was determined from a code developed by Dr Andrew Horsley at ANU. It numerically integrates a dipole over the solid angle of collection of the lens, which is dependent on the NA. This was done for a $\langle 100 \rangle$ and $\langle 111 \rangle$ orientated NVs with angles between the laser propagation direction and NV axis of 0° and 54°. A quadratic fit demonstrates the non-linear dependence of collection on NA.
lengths of the lenses $\theta_1/\theta_2 = d_2/d_1 = f_2/f_1$. This can be useful to optimally match the dynamic range of the galvos to the useful angular range of the objective lens or to expand the beam to fill the rear aperture of the objective lens. The lenses in the $4f$ system should be achromatic so both the green excitation and the red emission paths and focuses overlap.

A beamsplitter or dichroic mirror is used to separate the paths of the excitation and emission beams, after the beam splitter the excitation light is focused through a pinhole. The light after this pinhole is then collected through $f-2f$ lens system (figure A.5(a)) and focussed onto the detecting portion of the the APD. Between the dichroic or beamsplitter and the APD, a filter that strongly blocks the laser emission is added. Typically a long-pass optical filter at approximately 650 or 700 nm is used, the efficiency of a common Si APD has dropped off significantly ($\lesssim 10\%$) by about 900 nm. Creating a collection window between 700 and 900 nm. This counts most of the photons in the phonon-sideband of the NV emission. The long-pass filter is not chosen to be closer to the ZPL of NV$^-$ (637 nm) as might be expected. This is because the NV$^0$ emission sideband overlaps with NV$^+$ up to about 650-700 nm (see figure 2.3).

The excitation and emission confocal volumes must overlap, this is achieved by adjusting the position of the pinhole lens and keeping the laser path fixed. The alignment of the pinhole lens and APD can be a difficult process. The easiest method is to first roughly focus the pinhole lens by placing a mirror at the position of the objective lens so a collimated laser beam of full intensity is focussed back towards the pinhole lens. The pinhole is then optimized in $xyz$ by maximising laser intensity that is focused through the pinhole. Using an appropriate neutral density
A.2. **CONFOCAL MICROSCOPE**

filter, the laser travelling through the pinhole can then be reduced to as safe limit for
the APD and the counts on the APD maximised by adjusting the APD $xyz$ position. The
pinhole and the sensitive region of the APD chip are both small (each $\sim 20 \mu m$) so
careful optimisation and good quality micrometer stages are required. After this
rough alignment stage, the emission from some NVs or something else bright can be
focussed on with the microscope. Ideally the spot should be isolated and small, so
ture diffraction limited confocal volume of the microscope can be optimised upon. A
sample with known good single bright spots is helpful, if using an unknown sample it is
difficult to tell if the sample or the microscope is poorly performing. The surface
of the sample must be in focus, this is achieved by ensuring the collimated beam
reflected back off the surface is the same diameter (and divergence) as excitation
laser. If slightly defocussed from the surface the returning beam will be diverging
and expanding and could result in an inappropriate pinhole lens focus. Using these
bright spots near the surface, routinely re-focus the scanning confocal microscope
onto the centroid of a bright spot. The pinhole lens should be moved in discreet $z$
steps and re-optimised using $xy$ on the pinhole and re-focussing the centroid using
the scanning microscope. This has to be done iteratively, as each time $z$ is moved
on the pinhole lens it is likely that $xy$ will no longer be optimum due to some small
but likely non-concentric alignment of the components in the optical path. In this
way the global maximum $xyz$ of the pinhole lens can be found. The $xyz$ position of
the APD is not affected by the position of the pinhole lens as the pinhole is fixed
and acts as an effective point source of light, so this can be optimised separately.

The excitation laser is switched using and acousto-optic modulator (AOM).
These devices have a crystal which uses an acoustic wave to generate a change in the
refractive index of the crystal. The periodic pattern of the change in refractive index
acts as a Bragg grating and modulates the beams frequency, power and diffracts the
beam spatially into different directions. Since the frequency of the AOMs used is
$\sim 100$ MHz, the change in frequency of the laser is negligible ($f_{532nm} = 563$ THz
$\gg 100$ MHz). Using an aperture to block the zero-order diffracted beam and utilising
only the first order diffracted mode the light can be quickly switched on and off
by switching the power to the AOM. The intensity of the beam can be modulated
by adjusting the power to the AOM, for most lasers this is more convenient than
adjusting diode current to the laser. Another AOM is used to combine the extinction
ratio of each AOM, or more economically by double passing back into the same
AOM in a different polarisation and using a polarising beam splitter to separate
the uniquely polarised beams. This change in polarisation between in AOM passes
can be achieved using a quarter wave plate ($\lambda/4$), in each pass the laser picks up
APPENDIX A. EXPERIMENTAL DETAILS

A quarter wave polarisation change resulting in a net half wave change from linear horizontal or vertical. The extinction speed of the AOM is set by the speed of propagation of the acoustic wave through the beam diameter within the AOM crystal. This speed can be improved by focussing the beam to a smaller beam diameter, but care must be taken as to not exceed the power threshold of the AOM crystal. Confocal microscope systems are unlikely to exceed this power threshold but ensemble systems could reach this limit. Still the response of an AOM is quite slow, with an acoustic wave propagation of approximately 100s of mm/ns. For a focussed beam to 0.1 mm this is of order 10s of ns. Fortunately for NV− pulsed measurements the fluorescence is usually integrated for 100s of ns so the relatively slow rise time of the AOM is not significant.

A.3 Microwaves

A.3.1 Microwave structures

To drive the NV− centre’s ground and excited spin resonances microwaves are required. Ideally these microwaves should have the power capability to drive the spin with Rabi oscillations as fast as practically possible. For most pulse sources the minimum pulse time is approximately 1 ns, taking this minimum as the $\pi/2$ time, then the maximum desired Rabi frequency should be $1/4$ ns = 250 MHz. This is still far enough from the boundary of the rotating wave approximation (250 MHz < 2.87 GHz) to be desirable. The NV spin transition is coupled via a magnetic-dipole interaction, and as such the current produces a microwave frequency magnetic field to drive our spin resonances $\vec{\mu}_{NV} \cdot \vec{B}$. This is practically achieved by placing a small conducting wire(s) or conducting structure down upon the surface of the diamond. The closer we can put this conductor to our NV centre, the larger our field will be ($\sim 1/r^2$). Using larger wire is not suitable as the skin depths is $\sim 10\mu$m at 2.87 GHz so large wires offer no cross-sectional gain. More importantly, the field intensity at the surface of the wire drops off for larger radius wires, as the current density close to the diamond is reduced. The conductors are made by soldering a small $\sim 25 - 50\mu$m wire across the sample or by depositing a structure directly onto the diamond. This structure is then connected by silver paste, wire bonding or a mechanical connector to the surrounding conducting structure - usually a PCB which the sample is mounted on. In general, a microwave structure is more difficult to prepare, but will give a much stronger microwave to NV coupling. For similar ODMR signal contrast up to 20-30 dB ($10 - 100\times$) less power is needed for a NV
A.3. MICROWAVES

Figure A.6: (a) 3D image of deposited waveguide measured using laser optical profiler. (b) Darkfield microscopy image of the same deposited waveguide with shadow mask included.

directly next to a microwave structure $100\mu m \times 1.5\mu m$ compared to a $\sim 50\mu m$ wire.

Deposition of the microwave structure can be performed using thermal or e-beam evaporation techniques, the patterning can be achieved using optical lithography, e-beam lithography or shadow mask techniques. Due to its simplicity this work routinely used thermal evaporation and a shadow mask. The shadow masks used throughout this thesis were cut out of thin hardened steel plate using a wire cutting EDM machine. The resolution of this machine was limited to about $100 \mu m$ cuts, which was not ideally small enough but sufficient to get a considerable improvement in ODMR signal. Another approach investigated was to use a femto-second pulsed IR laser to ablate thin steel plate to create a shadow mask. This approach has showed feature sizes of $\sim 30\mu m$ and is relatively simple to perform and will be investigated more into the future. The deposition process consists of mounting the sample on a silicon wafer within a surrounding metal piece the same thickness as the diamond to mount the shadow mask upon. The sample, mask and silicon wafer were plasma cleaned in 100 W O2 plasma for 15 seconds. Then a 10 nm layer of Ti was thermally deposited by 1.5 microns of Cu also thermally. An example structure is shown in figure A.6

A.3.2 Amplifiers, switches and microwave sources

The output from the signal generator is passed to microwave with latching controlled by TTL signals from a pulse generating, with approximately 1 ns rise time. The output from these switches was passed to a either a 50W or 1W amplifier. The output from the amplifier is passed via a circulator past the sample to a $50\Omega$ load. To maximise signal throughput and reduce unwanted power reflections or loss, the
components must all be impedance matched to 50Ω. If a component is not designed to have a 50Ω impedance, then its length should be kept shorter than \(\lambda/4\). For a TEM mode in coaxial cable with a dielectric constant \(\epsilon\) is \(\lambda = v/f = c\sqrt{\epsilon}/f = 7.4\) cm \(\Rightarrow \lambda/4 = 1.8\) cm for 2.87 GHz and \(\epsilon \approx 2\) for PFTE insulator.

### A.4 Sample preparation

#### A.4.1 Cleaning

Sample cleanliness is paramount for good adhesion of deposited structures, to reduce contaminating fluorescence from dirt or ensure clean surfaces to limit the effects of dephasing from surface noise. The cleaning methods used in this thesis were,

- Soak in acetone, use very clean and dry glassware. Do not re-use glassware without cleaning. Sonicate and heat for more vigorous cleaning. Do not sonicate microwave structures as they can lift off.

- O₂ plasma etch at 100 W for 15 or 30 seconds - this was also done directly before microwave structure deposition.

- Piranha cleaning solution - 3 parts concentrated sulfuric acid (H₂SO₄) to 1 part hydrogen peroxide (H₂O₂). This is reacts strongly with organic materials and is useful for removing remnant glues or oil. Place diamond in a clean glass flask, add acid and then add the hydrogen peroxide slowly. Never add acid to peroxide. The reaction will finish within 10 minutes or so depending on exact amount of reactants. The reaction can get quite hot, so wait for the flask to cool down.

- Tri-Acid boil - boil diamond in equal parts of concentrated nitric acid (HNO₃), sulfuric acid (H₂SO₄) and perchloric acid (HClO₄). Place a spherical flask in a beaker containing some thermally conductive material (usually sand or silicon oil). Using a hotplate, heat the beaker and raise the temperature of the acid solution to approximately 200°C. Use a water cooled condensor coil above the spherical flask to collect and condense acid vapours back into the flask. Leave boiling for approximately 2 hours.

Acid and consumed piranha solution is disposed of by adding the concentrated acid to a large beaker of cold water (~1L) and adding small amounts of CaOH or NaOH to the water periodically checking the pH using Bromocresol purple indicator or pH
strips, once the solution is slightly basic stop adding the base. Always add the acid to a large amount of water, not water to acid as the reaction can boil the water. The neutralised solution can be poured down the sink with copious amounts of water.

A.4.2 Annealing

If implanted samples were required to be annealed after irradiation this was achieved in a tube furnace at 600-700°C for approximately 2 hours. The tube had flowing nitrogen gas running through it to purge air and oxygen from the furnace, as oxygen can rapidly etch diamond at these temperatures [236]. The nitrogen gas was passed through a desiccant to dry it prior to entering the tube. The nitrogen gas was also passed through a bubble valve at the outlet of the tube to prevent air getting into the tube through the outlet.
APPENDIX B

Analysis details

B.1 Double-clamped beam $\beta_n$ and $\alpha_{kn}$ coefficients

For a doubly clamped beam the mode shapes are described by

$$X_n(x) = C_n \left( \cos(\beta_n x) - \cosh(\beta_n x) - \frac{\cos(\beta_n L) - \cosh(\beta_n L)}{\sin(\beta_n L) - \sinh(\beta_n L)} (\sin(\beta_n x) - \sinh(\beta_n x)) \right),$$

(B.1)

where $\beta_n$ are the roots of $\cos(\beta L) \cosh(\beta L) = 1$, which can be solved numerically and are shown in table B.1.

$$\beta_n = \beta_1, \beta_2, \beta_3 \ldots$$

$$= 1.506\pi/L, 2.500\pi/L, 3.500\pi/L, \ldots$$

(B.2)

Equation 6.47 define the coefficients $\alpha_{kn}$ which satisfy $x_k = \sum_n \alpha_{kn}X^2_n(x)$. These are found from least squares regression as shown in figure B.1 and table B.1

<table>
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<tr>
<th>$n$</th>
<th>$\beta_n \times x/L$</th>
<th>$\alpha_{0n}$</th>
<th>$\alpha_{1n}$</th>
<th>$\alpha_{2n}$</th>
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<td>1.505619</td>
<td>0.126759</td>
<td>0.152069</td>
<td>0.081023</td>
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<td>-0.000320</td>
<td>-0.001176</td>
</tr>
</tbody>
</table>

Table B.1: Double clamped beam numerical parameters
Figure B.1: Upper plot shows the first $N = 10$ modes of $X_n(x)$ for the range $NL/(1 + N^2) < x < L/2$ as described by Haney et al [192]. Lower plot shows the function $x^k$ for $k = 0, 1, 2$ and the least-squares fit (dashed lines) using sums of the $n = 1, 2, \ldots, 10$ modes via $x^k = \sum_n \alpha_{kn} X_n^k(x)$. 
APPENDIX B. ANALYSIS DETAILS

B.2 MCD NV$^0$ $^2E$ Hamiltonian

The NV$^0$ ground state $^2E$ Hamiltonian as shown in equation 9.31.

$$H = \begin{pmatrix}
    Bg_\mu + Bl_\mu \cos \theta + 2\lambda \cos \theta & 2\lambda \sin \theta & \\
    2\lambda \sin \theta & -Bg_\mu + Bl_\mu \cos \theta - 2\lambda \cos \theta & \\
    0 & 0 & \\
    0 & 0 & \\
    0 & 0 & \\
    \vdots & \vdots & \\
    Bg_\mu - Bl_\mu \cos \theta - 2\lambda \cos \theta & -2\lambda \sin \theta & \\
    -2\lambda \sin \theta & -Bg_\mu - Bl_\mu \cos \theta + 2\lambda \cos \theta & \\
\end{pmatrix} \quad (B.3)$$

The eigenenergy solutions $E_{^2E,\uparrow\downarrow}$ to the above Hamiltonian are the same as shown in equation 9.32, where the $\uparrow\downarrow$ signifies orbit and the second $\pm$ signifies the upper or lower spin mixed branch

$$E_{^2E,\uparrow\downarrow} = -Bl_\mu \cos \theta \pm \sqrt{4\lambda^2 + (Bg_\mu)^2 - 4B\lambda B_\mu \cos \theta},$$

$$E_{^2E,\uparrow,\pm} = Bl_\mu \cos \theta \pm \sqrt{4\lambda^2 + (Bg_\mu)^2 + 4B\lambda B_\mu \cos \theta}. \quad (B.4)$$

and the eigenvectors, in the order $V_{^2E,\downarrow,-}$, $V_{^2E,\downarrow,+}$, $V_{^2E,\uparrow,-}$, $V_{^2E,\uparrow,+}$ using the same notation as the energies

$$\begin{align*}
    \left[ -\frac{1}{2\lambda} \left( -2\lambda \cot \theta + Bg_\mu \csc \theta - \csc \theta \sqrt{4\lambda^2 + (Bg_\mu)^2 - 4B\lambda B_\mu \cos \theta} \right), 1 \right] \\
    \left[ -\frac{1}{2\lambda} \left( -2\lambda \cot \theta + Bg_\mu \csc \theta + \csc \theta \sqrt{4\lambda^2 + (Bg_\mu)^2 - 4B\lambda B_\mu \cos \theta} \right), 1 \right] \\
    \left[ -\frac{1}{2\lambda} \left( -2\lambda \cot \theta - Bg_\mu \csc \theta + \csc \theta \sqrt{4\lambda^2 + (Bg_\mu)^2 + 4B\lambda B_\mu \cos \theta} \right), 1 \right] \\
    \left[ -\frac{1}{2\lambda} \left( -2\lambda \cot \theta - Bg_\mu \csc \theta - \csc \theta \sqrt{4\lambda^2 + (Bg_\mu)^2 + 4B\lambda B_\mu \cos \theta} \right), 1 \right]. 
\end{align*} \quad (B.5)$$

B.3 Error propagation and fitting

A large section of the data analysis in this work consisted of fitting spectral line-shapes to determine fundamental parameters. In every case this was performed
B.3. ERROR PROPAGATION AND FITTING

using the SciPy optimize Python library and the minimize function \cite{237}. This function can call a large variety of optimising algorithms. The bounded sequential least-squares programming (SLSQP) \cite{238} method was mostly used in this work. It optimizes a single scalar value so the sum of squares of residuals or the sum of squares of residuals divided by the standard error ($\chi^2$) of the fit is required. The SLSQP method allows for bounds to be placed on parameter estimates and is quite fast (directly calls Fortran sub-routines). It can perform badly if the initial parameters are poorly estimated. If there is no basis for an estimate of the fitting parameters, an annealing optimisation using the basinhopping SciPy optimize routine is used to sample over a large logarithmic range of estimate parameters. Once the range of parameter estimates was narrowed down, then the least squares SLSQP routine was called with the new partially optimised estimates.

In general the sum of squares function $M$ to be optimised is

$$M = \sum_i w_i (y_i - f(p_n, x_i))^2 \quad \text{(B.6)}$$

where the subscript $i$ denotes that the sum is performed over the length of the $x$ and $y$ points in the array. $f$ is the functional form trying to be fitted to the data $y$, and $p_n$ is an array of values to optimised. $w_i$ are optional weights to applied to the data if certain data points contain more merit than others.

For an example, if fitting a Lorentzian function to the data $f$ would be

$$f(p_n, x) = p_0 \frac{1}{\pi} \frac{\frac{1}{2}p_1}{(x - p_2)^2 + \left(\frac{1}{2}p_1\right)^2} \quad \text{(B.7)}$$

where $p_0, p_1, p_2$ are the amplitude, width and centre respectively of the Lorentzian function.

Although not necessary, it is advantageous for faster and more robust convergence to also describe the Jacobian of the optimised function $M$. In this case the Jacobian of $M$ is $\left[ \frac{\partial M}{\partial p_0} \ldots \frac{\partial M}{\partial p_n} \right]$. Applying the chain rule to B.6 gives the elements of the Jacobian,

$$\frac{\partial M}{\partial p_n} = \sum_i -2w_i (y_i - f(p_n, x_i)) \frac{\partial f(p_n, x_i)}{\partial p_n}. \quad \text{(B.8)}$$

Often it is not meaningful to obtain an absolute combined experimental/fit uncertainty in the fit from the covariance matrix output. A simpler method is the so called ‘bootstrap’ or Monte-Carlo method. In this method the function is fit
once firstly to determine the residuals. Then the input data is modulated by random Gaussian noise with a distribution width equal to the standard deviation of the residuals. If the experimental error of the inputs is known (reading error e.g. $1.0 \pm 0.1 \text{ mm}$), then random noise with a standard deviation equal to the experimental error is used. The fit procedure is repeated many times, each time with new randomly modulated set of data and a distribution of fit parameters is produced. The standard deviation of this collection of fit parameters is used as the uncertainty of the final values. The number of times to perform the bootstrap is determined by the convergence of the resulting parameters, usually this takes about 100-1000 iterations.

The weakness of the Monte-Carlo method is that it can over-estimate uncertainties and it relies on the assumption Gaussian noise. For the experiments conducted in this thesis Gaussian noise (photon shot-noise or PMT current noise) agrees well with the measured experimental error.
Bibliography


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