Chapter 3

Optical magneto-spectroscopy on the ground and excited state spin structure of c-axis divacancies in 4H-SiC

Abstract
Divacancies in SiC carry spins with long coherence times at cryogenic temperatures. Those oriented along the crystal growth axis (c-axis) share the symmetry of the well-known NV$^-$ center in diamond, and may provide an appealing alternative to NV$^-$ centers in quantum information applications: they are monodirectional, their operating wavelength lies on the edge of the telecom regime, and SiC is easily fabricated in bulk. This chapter shows investigations of the optical transitions of c-axis divacancy spin ensembles in 4H-SiC. By means of electron irradiation and annealing, the sample is made sufficiently optically thick for transmission spectroscopy. By applying a static magnetic field, and scanning the detuning of two lasers resonant with the zero-phonon line (ZPL), two distinct defects are found to be responsible for the inhomogeneously broadened ZPL. Though both share the known $S = 1$ ground state of $C_{3v}$ symmetry with 1.3 GHz zero-field splitting, their excited states are markedly different: these are still $S = 1$ spin triplets, but only one is of $C_{3v}$ symmetry, while the other’s is as yet unclear. Regardless, it is shown that by working on the low-energy side of the inhomogeneously broadened ZPL and tuning direction and strength of the magnetic field, these divacancies provide a promising candidate system for all-optical applications based on electromagnetically induced transparency.
3.1 Introduction

In search of building blocks for quantum information processing, silicon carbide is turning out to provide a promising and versatile toolbox. Many distinct point defects carry spins, long-lived and long-coherent, with a wide range of other favourable properties, depending on the choice of defect. For example: PL4 divacancies in 4H-SiC offer a flexible route to polarizing the ground state spin of mono-directional ensembles [48]; an ensemble of about 1000 6H-SiC PL6 electron-nuclear spin pairs have been entangled at room-temperature [49]; carbon antisite-vacancies in 4H-SiC were shown to act as bright single photon sources at 300 K [13].

Out of all the point defects in SiC potentially suitable for quantum applications, divacancies pointing along the c-axis (growth axis of the crystal) are a particularly close cousin to the untill now most widely studied and applied [25, 29, 50, 51] color center spin system: the NV$^-$ center in diamond. Sharing the NV-center’s $C_{3v}$ point group symmetry [52], and having been shown to host a long-coherent $S = 1$ ground state spin [10], c-axis divacancies immediately seem promising candidates for all-optical quantum applications. An obviously appealing feature of these defects is their pointing in only one direction, reacting equally to electric, magnetic, and strain fields, simplifying their use in ensemble-based approaches [3]. This is also a clear potential advantage over the basal-plane divacancies covered in chapter 2), which have degenerate defect orientations at zero external field, and lower $C_{1h}$ symmetry.

If the analogy with the NV-center holds, the optically excited state of c-axis divacancy spins could take several forms. Due to coupling of degenerate electronic states to vibrational modes of the lattice, the $C_{3v}$ symmetry is lowered, an effect described by the Jahn-Teller theorem [50, 53, 54]. For the NV$^-$ excited state manifold, this yields an orbital doublet, spin $S = 1$ system. For high enough temperature, coupling between the orbital excited states then causes the system to rapidly switch between these states, so that on any appreciable timescale the excited state appears to have retained $C_{3v}$ symmetry. For low enough temperature this switching is frozen, and the lower symmetry can be observed. If, and at what temperature this change would occur for divacancies in SiC is currently unknown. The main motivation of this chapter is to acquire detailed knowledge of these excited state sub-levels for divacancy spins, and the transition rules for excitation into them from the ground state sub-levels. This is an essential step towards designing and optimizing many optical quantum applications of these
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defects, and can help understanding of color center spins in general.

While there exist in principle hundreds of distinct c-axis divacancies throughout the different polytypes of SiC (in nH-SiC there are in general n divacancies with a unique local crystal environment [40]), this chapter will focus on the c-axis divacancies in electron-irradiated 4H-SiC. Due to the irradiation and subsequent annealing, the divacancy concentration was sufficient to make the 2 mm wide sample absorbing enough for ensemble transmission spectroscopy of divacancy transitions.

We first present single-laser studies that characterize the inhomogeneous broadening of the optical transitions. Next, dual-laser experiments for extracting homogeneous signatures of the spin levels from the ensemble are presented. By combining these measurements with a static magnetic field, and performing additional measurements on optical bleaching (see chapter 2, section 2.11), insights into the spin structure of the defects were achieved.

The unexpected result is that there are two different excited states with $S = 1$ with nearly the same optical transition energies, belonging to different physical defects. One of these behaves as expected for a defect with $C_{3v}$ symmetry and no visible Jahn-Teller distortion, but the other does not. To then achieve homogeneous interaction of a particular homogeneous sub-ensemble with the optical fields, the alignment and strength of the static magnetic field is carefully optimized. This clears the way for all-optical quantum memory applications with defect ensembles in 4H-SiC.

3.2 C-axis divacancy spins in irradiated 4H-SiC

The two distinct c-axis divacancies in 4H-SiC, called PL1 and PL2, are known to have direct optical transitions to excited states, which are very close to each other in energy. The main panel in Fig. 3.1 shows the photoluminescence (PL) collected by illuminating the material with 1.146 eV photons at 20 K, exciting the phonon sidebands of PL1-3 (no magnetic field present). This excitation energy is just low enough to avoid exciting the PL4 basal plane-oriented divacancies at 1.15 eV, which would otherwise dominate the spectrum, as shown in chapter 2. With this excitation energy, the zero phonon lines (ZPL) of both PL1 and PL2 are visible at 1.094 eV, though the resolution of the spectrometer used is insufficient to resolve both lines. Also visible are the emitted phonon sidebands (PSB) of both defects. These cover a broad range of energies lower than the ZPL, where part of the excited state energy is emitted as a photon, and the remainder as
phonons. A measure of the potential efficiency of a defect in applications is how much light is emitted in its ZPL compared to the PSB: for 4H-SiC divacancies 4±1% of light goes into the ZPL, which is a little higher than for the NV$^-$ center in diamond.

Figure 3.1: PL and absorption of c-axis divacancies. An excitation laser of 1.146 eV illuminated the sample at 20 K, and PL from c-axis divacancies is collected by an Ocean Optics NIRQuest spectrometer, with 3 meV resolution. The zero-phonon lines of PL1 and PL2 (the two types of c-axis divacancies overlap due to this resolution, as do their phonon sidebands. The inset shows the voltage of an amplified InGaAS photodetector, recording the transmission of a CW narrow-linewidth diode laser that is scanned over the ZPL of PL1 and PL2. PL1 and PL2 are here clearly separated by 400 GHz, and inhomogeneously broadened, with an FWHM here on the order of 100 GHz.

In the previous chapter PL (and the associated technique PL excitation, or PLE) was used, rather than transmission studies, to detect the interaction of divacancy spins with light, together with a sample shaped and coated to enhance PL collection. Extreme sensitivity was needed due to the low native concentration of divacancies in commercially available SiC (estimated at or below $10^{13}$ cm$^{-3}$). For practical implementations, this is not good enough: the sample needs to be optically thick, so that for instance a single photon can be reliably absorbed, instead of this failing to happen 99% of the time. To boost the divacancy concentration, the sample used here was irradiated with a 2 MeV electron beam,
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Dose $8 \times 10^{18}$ cm$^{-2}$. This creates a broad array of lattice defects, so the sample was subsequently annealed at 750 °C for 15 minutes, to let single carbon and silicon vacancies diffuse and combine into energetically favourable divacancies. By this method, the total divacancy concentration goes up, and from our measurements was estimated to be in the range of $10^{15}$ to $10^{17}$ cm$^{-3}$.

In the inset in Fig. 3.1, the signal from an InGaAs amplified photodiode placed behind the sample is shown, with a single laser passing through the sample falling on it. The laser wavelength is scanned across the ZPL peak from the main panel, again at 20 K and zero magnetic field. This way, the measurement resolution is set by the laser linewidth (sub-MHz), and the ZPL for both PL1 and PL2 is clearly resolved, separated by 400 GHz. From here out, $f_0$ is defined as the center of PL2, which is the defect of focus in this chapter (see section 3.10 for information on PL1). We verified that only the component of the laser polarized orthogonal to the c-axis was absorbed, so the optical dipoles of PL1 and PL2 lie in the basal plane.

For both defects the ZPL has a FWHM of about 100 GHz, which is broad compared to the expected homogeneous linewidths in the order of 100 MHz. This width is 5x larger than the non-irradiated samples studied in chapter 2, strengthening the notion the broadening is caused by internal strain. Working with defect ensembles in a bulk crystal, the ZPL is typically inhomogeneously broadened due to strain, interaction with impurities - imperfections of the host material as opposed to vacuum. On the positive side, ensembles can benefit from collective enhancement, which offers a way around having to engineer complicated and error-prone cavities to work with single (fundamentally homogeneous) defects. In the remainder of this chapter, two carefully detuned lasers are used to interact exclusively with homogeneous sub-ensembles in the presence of inhomogeneity. Due to the concentration increase by a factor 1000 compared to the material of chapter 2, and the broadening by a factor 5, the defect count in the homogeneous sub-ensembles is increased by a net factor 200 compared to the non-irradiated samples of chapter 2. This is a significant improvement which can make the difference between spins signatures being readily visible in transmission or not.

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By cooling the sample so that transition linewidths become narrower than the spin sub-level splittings, the spins can become polarized by applying a narrow-
linewidth CW laser to individual transitions (at elevated temperatures, a single laser excites many broad and overlapping transitions). This effect is called optical spin pumping (OSP). By applying two lasers with a particular detuning, the OSP is lifted, for situations where the two lasers excite from all ground state sub-levels simultaneously. We call the homogeneous PLE features seen at these resonance conditions spin-related emission (SRE) features. In chapter 2, this phenomenon was used together with an external static magnetic field to unravel the spin structure of basal-plane divacancies, and a similar approach is used here. In this chapter, they will be referred to as spin-related absorption (SRA) features, since absorption is the quantity under study.

If the excited state is a spin triplet (or if it consists of more than three levels of which some subset shifts and (anti-)crosses like a spin triplet under magnetic field), a promising field orientation for magneto-spectroscopy can be chosen to optimize SRA. Since c-axis divacancies are mono-directional, only one angle is used to describe this orientation: the angle \( \phi \) between c-axis and magnetic field. It must be emphasized that this approach is based on an initial assumption about the form of the Hamiltonian, but our results will show that it is a valid approach.

The Hamiltonian for a \( C_{3v} \) spin \( S = 1 \) system in an external magnetic field is

\[
H_{g(e)} = g_{g(e)} \mu_B \vec{B} \cdot \vec{S} + \hbar D_{g(e)} S_z^2,
\]

where \( g_{g(e)} \) is the g-factor for ground (excited) state, \( \mu_B \) is the Bohr magneton, \( \vec{B} \) is the magnetic field, \( \vec{S} \) the unitless spin \( S = 1 \) operator, and \( \hbar \) Planck’s constant. \( D_{g(e)} \) is the zero-field splitting parameter in Hz due to spin-spin interaction. \( D_g \) is known to be 1.305 GHz from ODMR experiments, and \( D_e \) was recently reported to be on the order of 770 MHz. The \( z \)-axis points along the c-axis (its direction does not matter). The angle \( \phi \) governs how the spin energy levels will shift with the field (determining transition frequencies), and whether there will be avoided crossings upon mixing of the spin eigenstates (altering transition dipole strengths via the Franck-Condon principle for spin, see chapter 2, section 2.8). This is shown for both ground and excited state in Fig. 3.2a for \( \phi = 57^\circ \) and \( \phi = 33^\circ \), the two angles used in experiments throughout the remainder of this chapter. The spin states are labeled \( |g_i\rangle \) and \( |e_i\rangle \), with \( i = l, m, u \), as in chapter 2.

To achieve strong absorption with three long-lived ground state levels and only two lasers to excite from them, it is important that for a given homogeneous sub-ensemble such as depicted in Fig. 3.2a, a single laser is made resonant with
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Figure 3.2: Model predicting optimal angle $\varphi$ for SRA. a) Spin energies for ground and excited state calculated from Eq. 3.1 for two angles $\varphi$ between magnetic field and c-axis, $D_g = 1.3$ GHz, $D_e = 500$ MHz, and $g_{g(e)} = 2$. The bendings are due to avoided crossings, which depend on $\varphi$. The frequency $f_0$ is the peak of the inhomogeneous PL2 ZPL, defined in the inset of Fig. 3.1. b) Transitions calculated from a) for $\varphi = 33^\circ$. The linewidth is proportional to the predicted dipole strength, based on a Frank-Condon principle for spin. Blue involves $|g_l\rangle$, black $|g_m\rangle$, red $|g_u\rangle$. Transition frequencies cross, but none overlap fully, predicting poor SRA at most fields. c) Like b), but for $\varphi = 57^\circ$. Now pairs of transitions do overlap for a large range of magnetic field strength (the overlaps are labelled O$_1$ and O$_2$), predicting clear SRA at this magic angle. d) Spin pumping for the two schemes O$_1$ and O$_2$ defined in c). Orange arrows indicate the identical transitions, driven by a single laser (addressing two ground state levels). Green dashed transitions can give SRA, pumping from the third ground state level. Four distinct detunings can give SRA, labelled $\Lambda_i$ or $\Pi_i$, depending on the resulting pumping scheme.

two transitions. Otherwise, the spin is polarized into the third off-resonant level after only a few excitation cycles, and not interacting with the applied laser fields anymore. From Eq. 3.1 with $D_g = 1.305$ GHz and $D_e = 500$ MHz, the nine possible transitions are calculated and depicted in Fig. 3.2b-c, for $\varphi = 33^\circ$ and
\( \varphi = 57^\circ \), respectively. Blue lines are transitions out of \( |g_l\rangle \), black out of \( |g_m\rangle \), and red out of \( |g_u\rangle \). The width is proportional to the dipole strength, taken to be the inner product of ground and excited state spin energy eigenstates (Frank-Condon principle for spins).

It is found that only for \( \varphi \) values close to \( 57^\circ \), two pairs of transitions overlap over a wide range of field strengths. These two overlap regions are labeled \( O_1 \) and \( O_2 \) in Fig. 3.2c. If \( D_e \) becomes larger, the start of overlap \( O_2 \) gradually moves to higher magnetic fields. However, for any \( D_e < 100 \) GHz, overlap \( O_1 \) remains, for magnetic fields below 100 mT (more than will be needed in these experiments). Thus, the angle \( \varphi = 57^\circ \) should yield strong SRA features for a wide range of magnetic fields, regardless of the exact zero-field splittings in the excited state, as long as (a subset of) the excited state levels behaves as a spin triplet as in Eq. 3.1 under magnetic field.

In Fig. 3.2d three ground state and three excited state levels are drawn for excitation of both overlaps \( O_1 \) and \( O_2 \), for a magnetic field large enough for the overlaps to exist. Orange arrows represent the two identical transitions being addressed by a single laser (thus addressing two ground state levels). The green dashed arrows are transitions driven by the second (detuned) laser that should yield SRA features, by driving transitions from the third ground state level. These transitions are labelled with a \( \Lambda \) when the green transition couples to the same excited state level as one of the orange transitions. In such a \( \Lambda \) system, quantum interference may take place in the system’s driven dynamics, which is a key ingredient for many quantum applications of these defects, and is discussed in more detail in chapter 4. If the system is not a \( \Lambda \) system, it is termed a \( \Pi \) system. Since SRA features only show the difference between transition frequencies, the Lambda systems in \( O_1 \) and \( O_2 \) are indistinguishable in these measurements. That leaves a total of four expected SRA features at \( \varphi = 57^\circ \), labelled \( \Lambda_1, \Lambda_2, \Pi_1, \) and \( \Pi_2 \).

### 3.4 Method: dual-laser transmission spectroscopy

To improve the dual-laser measurements in terms of signal-to-noise by more than a factor 10 compared to the PLE from chapter 2 (or equivalently measurement speed by a factor 100), the TEM\(_{00}\) laser beams are spatially separated behind the sample. They cross near-parallel to within \(< 5^\circ \) inside the sample, as is shown in Fig. 5.1. The sample thickness \( d = 2 \) mm, and the beams are focussed by a lens with \( f = 15 \) cm focal length to a diameter of 70 \( \mu \)m. The detuned laser beam is
generated from the first using an Electro-Optic Modulator, giving kHz precision in two-laser detuning, and intrinsic phase coherence (a substantial improvement over the 1 MHz resolution obtained in the basal-plane divacancy measurements in chapter 2, where two different lasers were used). One beam passes through a chopper wheel rotating at 270 Hz (the near-horizontal periodic beam in Fig. 5.1). When this beam (chop beam) is blocked by the chopper, the other beam (probe beam) pumps the spins it encounters into off-resonant long-lived states within 100 ns, and after that passes through the sample undisturbed: transmission is near-perfect (besides the reflection of the sample surfaces). On the other hand, when the chop beam passes the chopper (and has the proper frequency with respect to the probe beam), it counteracts the spin pumping, leading to reduced transmission of both lasers.

**Figure 3.3: Experiment schematic.** Chop beam, probe beam and repump beam cross in the 4H-SiC sample under a small angle ($< 5^\circ$, exaggerated in this figure for clarity), exciting divacancies (yellow dots). Due to optical spin pumping being turned on and off as the chop beam turns off and on, respectively, the probe beam transmission is modulated with the chop frequency. Behind the sample, the chop beam is blocked by an iris, and the probe beam is picked up by an InGaAS photodiode. Its signal is passed to a lock-in amplifier, isolating the modulation signal. The sample has a thickness $d = 2$ mm, and may be rotated to vary the angle $\varphi$ between c-axis and magnetic field.
The modulation of the probe beam was typically only a fraction of its amplitude, while the chop beam was modulated by 100% of its amplitude. Filtering out the chop beam before detection thus removes a large background signal, improving the sensitivity of the measurement. Since the laser frequencies differ in the range of 1 MHz to several GHz, it is not possible to adequately separate the beams using simple wavelength filters, and impractical to do so using cavities. Also, due to the birefringence of SiC and the optical dipoles of the divacancy spins, separating the beams after the sample based on polarization does not work [55]. By placing an iris behind the sample, making use of the small angle between the beams, the chop beam could be spatially filtered out, so that the amplified InGaAs photodetector detects only the probe beam.

Before entering the cryostat, intensity noise below 1 MHz in the probe beam is actively filtered out by a noise eater (feedback loop consisting of a photodiode and liquid crystal attenuator). Looking for a 270 Hz component in the photodetector signal behind the cryostat using a lock-in detector, any signal found is therefore due to the lasers interacting with the same divacancies, as described above. By increasing the intensity of the chop beam compared to the scan beam, this 270 Hz modulation of the probe beam can become very large compared to the residual 270 Hz noise in the detector signal. This modulation is, in case the chop laser increases absorption, 180° out of phase with the chopper wheel opening. In this chapter, the absolute value $R$ of the lock-in amplifier is used as a measure of the SRA. We never saw signals with a phase of 0°.

Finally, an additional repump laser is applied, at 770 nm (also filtered out before the photodiode by the iris) to counteract optical bleaching by the other lasers. After several excitation cycles, the divacancies can switch into another, off-resonant charge state. This laser serves to switch them back from that state (it was verified not to have a noticable effect on the results presented in this chapter).

### 3.5 Experimental results and modelling

#### 3.5.1 Spin-related absorption features: two groups

In Fig. 3.4, both the direct photodiode signal and the absolute value $R$ of the lock-in signal are shown, from two 700 nW CW diode lasers. One laser frequency was fixed to a particular carrier frequency $f_C$ on the ZPL of PL2, and for the other laser the detuning from $f_C$ was scanned. The maximum of the inhomogeneously
broadened ZPL is defined as $f_0$, as shown in the inset of Fig. 3.1. For the blue traces $f_C$ was tuned to the high-frequency slope of the inhomogeneous ZPL, while for the red traces $f_C$ was tuned to the low-frequency slope.

Figure 3.4: Direct and lock-in detection of SRA features. The top traces are direct transmission of the probe laser through the sample as a function of two laser detuning, for two different $f_C$ (the peak frequency of the ZPL of PL2, as defined in the inset of Fig. 3.1). $T = 4$ K, $B = 9$ mT, $\varphi = 57^\circ$. Here 100% transmission is defined as the amount of light passing the sample when the lasers are not on the ZPL of PL2. The bottom traces are the lock-in signal obtained from the direct transmission signal, showing superior signal-to-noise for SRA. The chopper frequency was 270 Hz, integration time 7 seconds per datapoint. Seven SRA peaks are visible in the lock-in signal, numbered and indicated by grey lines. This is more than the four lines predicted in section 3.3. Also, the peak heights depend strongly on the carrier frequency $f_C$.

A small magnetic field of 9 mT was applied, at an angle of $\varphi = 57^\circ$. This field was applied for two reasons. Firstly, it lifts spin energy level degeneracies, showing more separated SRA features. Secondly, it mixes the ground and excited spin states, making transition dipoles proportional to $\langle g_i | e_j \rangle$ non-zero (which is depicted as a broadening of the transitions in Fig. 3.2b-c with magnetic field). If
more transitions are dipole-allowed, more pairs of transitions can produce SRA features. In Fig. 3.4, the temperature was 4.2 K: it was observed that only below 14 K the linewidths are narrow enough for the SRA features to become visible. Below 6 K the homogeneous SRA features have a typical FWHM of 120±20 MHz, implying excited state lifetimes on the order of 10 ns. Clearly from Fig. 3.4, the lock-in technique greatly improves over the DC measurements, showing smooth features which are obscured by noise in the direct transmission signal. Here, the integration time was 7 seconds per datapoint, and even averaging over several minutes the direct transmission trace was much noisier than the lock-in trace. It is worth emphasizing here that the lock-in signal $R$ is proportional to the absorption of the probe laser in the sample, and hence lock-in SRA features have an opposite sign compared to those in direct transmission.

There are seven SRA features visible in Fig. 3.4, indicated by grey lines and numbered from low to high detuning. In section 3.3 it was predicted that for a triplet ground and excited state with spin Hamiltonians as Eq. 3.1, regardless of the exact value of the zero-field splittings, only four SRA features should appear. A second departure from the triplet-triplet model is that the amplitudes of all seven features depend strongly on $f_C$: features 1, 2 and 4 dominate at high $f_C$, while features 3, 5 and 6 are clearest at low $f_C$. This is in stark contrast to basal-plane divacancies, where we never observed an influence of inhomogeneity on the observed features. To understand this behaviour, the measurement from Fig. 3.4 was repeated for the range of $f_C$ that fully covers the inhomogeneous ZPL. The result of this measurement is shown in Fig. 3.5. The temperature was held at 4.2 K, magnetic field was 9 mT, and $\varphi$ was 57°. For all these features, it was observed that they vanish when either beam is polarized parallel to the c-axis.

The seven dark vertical lines in Fig. 3.5 are the seven peaks from Fig. 3.4, showing a change in amplitude as $f_C$ is scanned over the entire inhomogeneous ZPL, with an FWHM of 80 GHz. Since all the lines appear perfectly vertical, there is no discernible influence of inhomogeneity on the spin structure inside the ground or excited states, i.e. the zero-field splittings appear constant. This implies that the broadening of the ZPL only reflects inhomogeneity in the energy difference between ground and excited state. What stands out, is that the features appear to fall into two groups, peaking at $f_C = f_0 - 18.5$ GHz and $f_C = f_0 + 11.5$ GHz, 30 GHz apart. They will be referred to as group A and group B, as labelled in Fig. 3.5. Group A consists of four features of which two are faint (A1 and A4) and two are prominent (A2 and A3). Group B consists of three
Figure 3.5: Carrier frequency dependence of SRA signals. The grayscale presents the signal of SRA features, as a function of both the single-laser scan frequency $f_C$ (scanned for over 100 GHz), and the two-laser detuning. Two groups of SRA features are visible, labeled group A and B, peaking at $f_C = f_0 - 18.5$ GHz and $f_C = f_0 + 11.5$ GHz, respectively. The features seem almost perfectly vertical, so the zero-field splittings of ground and excited state are constant over the entire inhomogeneous spectral width of the ZPL, and only the energy splitting between ground and excited state changes.

about equally clear features. The appearance of these two groups persisted when measuring on several positions on the sample. The following section will show that groups A and B do not originate from the same defects, neither in terms of spin structure or actual physical divacancies.

3.5.2 Proving the SRA groups come from different defects

To explain the separation of SRA features into two groups, a possibility is that the features in group A result from one subset of excited state levels, and those in group B from a second subset of excited state levels from the same defect, 30 GHz higher in energy. These subsets of levels could originate from a Jahn-Teller distortion, and be shifted apart by lattice strain. To test this hypothesis, a method is needed to tag the defects by interaction with one SRA feature group,
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and look for this tag in the other group. A suitable tool for this is the optical bleaching effect, where defects switch their charge state, becoming far off-resonant with the lasers (see 2, section 2.11). This could indeed be applied for c-axis divacancies.

![Figure 3.6: SRA feature correlations by spectral hole burning.](image)

Two-laser transmission studies at $T = 4.2$ K, $B = 9$ mT, $\varphi = 57^\circ$. The plot depicts scans of $f_C$ over the SRA features shown in Fig. 3.5, with the two-laser detuning kept fixed (i.e. vertical cuts through Fig. 3.5). The traces show whether SRA features are caused by the same physical defects, by means of spectral hole burning. This correlation is tested by first burning a spectral hole in one SRA feature, and then seeing if the hole also appears in a scan of $f_C$ over another SRA feature. The black trace is a reference of feature A2 before hole burning; the blue trace shows the shape of a spectral hole; the green trace proves different features in group A come from the same defect sub-ensemble; the lack of a hole in the red trace proves that groups A and B do not originate from the same defect sub-ensemble.

Initially, the chop laser and probe laser are tuned to one of the seven SRA features, for example A2 (so the chop laser frequency $f_C = f_0 - 18.50$ GHz, and the probe laser frequency $f_p = f_0 - 18.50 + 1.23$ GHz). Then the repump laser is turned off. Without the repump, the chop and probe laser cause the defects to switch to an off-resonant charge state, and a spectral hole is formed at this particular $f_C$. The defects were seen to stay off-resonant for hours, i.e. the other charge state is stable. When the signal has decayed to over 50% (taking about 3 minutes with 8 W cm$^{-2}$ laser powers), the lasers are attenuated by a factor 300, so the bleaching becomes very slow (taking more than a day to reach 50%). Next, with a fixed two-laser detuning, $f_C$ is scanned over any SRA feature from Fig. 3.5, for instance A3. Taking only several minutes, this causes no significant
extra bleaching, so it is in effect a non-invasive measurement. If the spectral hole created in A2 is also seen in A3, this proves the SRA features belong to the same physical ensemble of defects. If no change in A3 is seen, the features cannot come from the same ensemble of defects.

In Fig. 3.6, the result of these correlation measurements are shown (temperature is 4.2 K, magnetic field 15.4 mT, and $\varphi$ is 57°). The lasers were held to within 5 MHz in absolute frequency while the spectral hole was being burned. The black trace is the reference trace, showing the inhomogeneously broadened profile of feature A2. The blue trace shows the trivial case of correlation, where a spectral hole is first burned in B1, and then a scan over B1 itself shows the lineshape of a spectral hole. A clear dip of over 50% of the peak height is visible, with a FWHM of 4.5±0.2 GHz. To prove that different features can be correlated by this method, the green trace shows a spectral hole measured in feature A3, after feature A2 was used to burn the hole. Again a clear dip is seen, with FWHM of 4.0±0.2 GHz. However, when looking for correlation between the two groups, by burning a hole in feature B1, and scanning $f_C$ over feature A2, no spectral hole appears, as shown by the red trace. This proves SRA features grouped as A and B belong to different physical defect sub-ensembles (which could both still consist of c-axis divacancies, but with different spin levels and transitions).

### 3.5.3 Identifying group A with magneto-spectroscopy

Having shown that groups A and B come from different spin systems, this section will show that the four features in group A can be well explained by the four SRA features $\Lambda_1$, $\Lambda_2$, $\Pi_1$ and $\Pi_2$ predicted in section 3.3 for an $S = 1$ ground state and $S = 1$ excited state described by Eq 3.1. The analysis is based on the data in Fig. 3.7. With the carrier frequency fixed at $f_C = f_0 - 9$ GHz to show maximum lock-in signal from group A, the detuning is scanned as in Fig. 3.4. The magnetic field strength is varied between 0 and 70 mT, causing the spin sub-levels in ground and excited state to Zeeman shift. Temperature is kept at 4.2 K.

In Fig. 3.7a, the result of this scan is shown for $\varphi = (57\pm1)^\circ$, and a carrier frequency $f_C = f_0 - 9$ GHz, predominantly showing the features of group A. The SRA features are labelled as in Fig. 3.5. The black lines are fits of the three expected features $\Pi_1$, $\Lambda_1$ and $\Lambda_2$ (as defined in Fig. 3.2d), calculated from Eq. 3.1 by taking the differences between the two transitions involved (so the difference between the traces in Fig. 3.2c). The fitting approach was aimed at minimizing the distance from the model to the lock-in signal maxima.
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Figure 3.7: Magneto-spectroscopy of group A SRA features. a) Probe laser absorption measured by lock-in detection, as a function of two-laser detuning and magnetic field strength, for $\varphi = 57^\circ$, the magic angle predicted to give strong SRA in section 3.3. The four features from group A are predominantly visible due to the choice of $f_C$, and are labelled as in Fig. 3.5. The black and red lines are fits of the four SRA features $\Lambda_1, \Lambda_2, \Pi_1$ and $\Pi_2$ defined in Fig. 3.2, calculated with Eq. 3.1 (details in main text). b) Measurement like a), but with $\varphi = 33^\circ$ (rotated away from the magic angle). SRA features become less clear, as expected, yet are still visible. Black and red lines are model predictions and fits (details in main text). From the fits to both these data sets, the ground and excited states are found to be $S = 1$ triplets, with zero-field splittings $D_g = (1310 \pm 10)$ MHz, and $D_e = (500 \pm 50)$ MHz.

Features A2 and A3 are well fit by $\Lambda_1$ and $\Lambda_2$ from the model, when $D_g$ is fixed at 1.305 GHz, and $g_g$ and $g_e$ are kept equal, giving best results when set to $1.87 \pm 0.04$. Since A2 and A3 originate at the same detuning at zero magnetic
field, two of the ground state levels are degenerate at zero field, consistent with the assumption of $C_{3v}$ symmetry. Since Λ systems are independent of the excited state splittings, only feature A1 can give information on the excited state zero-field splitting $D_e$. This is complicated by A1 being invisible at magnetic fields below 20 mT, and even at higher fields A1 is dim compared to lines A2 and A3. This is in sharp contrast to SRA seen in basal-plane divacancies, where Π systems typically show up much more strongly, dominating magneto-spectroscopy scans (see chapter 2, section 2.2). However, fitting the predicted Π$_1$ line to feature A1, an upper limit of $D_e = 550$ MHz can still be obtained (the black fit covering A1). The model outcome for a larger value of $D_e = 650$ MHz is shown in dashed red. It clearly lies further away from feature A1, both at the line crossing at 22 mT, and towards 70 mT where A1 becomes more visible. The reason neither black or red fit seems perfect by eye near 70 mT, is that there is some residual SRA from feature B2 on the high-detuning side, which causes A1 to seemingly broaden towards higher magnetic field. Lastly, feature A4 is hardly visible for these fields and detunings, but has been confirmed to overlap well with where Π$_2$ should lie at lower carrier frequency and higher two-laser detunings (not shown). Feature A4 being dim compared to the other three features is consistent, considering the transitions involved are weaker (see predicted widths of the transitions in Fig. 3.2c: A4 is formed by the transitions from overlap O$_2$, together with the thinnest topmost blue transition).

To further confirm this identification, the measurement from Fig. 3.7a is repeated at a different angle $\varphi$ between field and c-axis, to see whether lines A1-A3 Zeeman shift as expected. The result is shown in Fig. 3.7b, where $\varphi = (33\pm1)^\circ$. Away from the magic angle of $\varphi = 57^\circ$ there is no consistent overlap of transitions for all magnetic field strengths. This indeed leads to less clear SRA features in Fig. 3.7b, supporting that $\varphi = 57^\circ$ is near-optimal. The black lines covering features A2 and A3 are now not fits, but predictions of the model where lines Λ$_1$ and Λ$_2$ should lie for this angle $\varphi$ based on the parameters from fitting Fig. 3.7a. The SRA features A2 and A3 can still be recognized in the lock-in signal, matching closely with the model predictions.

Since the overlap of transition frequencies O$_1$ (defined in Fig. 3.2) is no longer present at this angle, the line Π$_1$ is expected to split in two lines, of lower visibility than at $\varphi = 57^\circ$. Predictions for these two lines are drawn in black, both starting near 800 MHz at zero field. Looking closely, this splitting is also visible in the lock-in signal between 20 and 30 mT. Fitting these two lines yields a lower limit of $D_e = 450$ MHz. To support this, drawn in dashed red in Fig. 3.7b is the
model outcome for $D_e = 350$ MHz. For this value, as can be seen in the white box where the contrast has been increased by a factor 2 for clarity, the model does not agree with the data anymore, missing the peaks in SRA. Combining the limits for $D_e$ found from Fig. 3.7a-b, the best estimate from this data of $D_e$ for PL2 divacancies is $D_e = (500\pm50)$ MHz.

If the symmetry of the excited state is in fact lower than $C_{3v}$, the Hamiltonian from Eq. 3.1 needs to be modified to include zero-field splitting terms orthogonal to the c-axis:

$$H_{g(e)} = g_{g(e)}\mu_B \vec{B} \cdot \vec{S} + hD_{g(e)}\vec{S}^2 - hE_{x,g(e)}(S_x^2 - S_y^2) + hE_{y,g(e)}(S_xS_y + S_yS_x).$$  (3.2)

For the ground state, $E_{x,g}$ and $E_{y,g}$ are clearly zero from the data, since features A2 and A3 are degenerate at zero field. For the excited state, a similarly strong claim cannot be made, since the feature A1 is not visible at low magnetic fields. Small values of $E_{x,e}$ and $E_{y,e}$ are most easily identified at low fields, where the Hamiltonian is dominated by the zero-field splittings, and not the Zeeman term. From what is visible of feature A1, the fits do not become significantly better or worse for values of $E_{x,e}$ and $E_{y,e}$ below 0.1 GHz. Hence, the data is consistent with a $C_{3v}$ symmetry for the excited state, but does not rule out a small deviation from $C_{3v}$.

### 3.5.4 Explanations for the suppressed Π₁ SRA feature

From the simple model of optical spin pumping described in chapter 2, section 2.8, which successfully described the SRA features for basal-plane divacancies in chapter 2, the feature A1 is expected to dominate the other features. This is because A1 is formed by driving the three transitions with the largest optical dipoles, $\langle g_i | e_i \rangle$: the Π₁ system predicted in section 3.3. Instead, in the data, A1 is relatively small, and even invisible at low fields. To explain the apparent suppression of this Π system, the cause seems likely to lie with the transition that only A1 uses: that from $|g_l\rangle$ to $|e_l\rangle$. Considered here are three mechanisms that could be responsible for this transition behaving differently than expected: closed transitions, intersystem crossing to a metastable singlet state, and forbidden transitions (without going into detail on its possible origins).
Closed transitions

The first cause of the weaker SRA signal for the Π\textsubscript{1} system is the possibility of a closed transition, as is known to exist in the similar NV\textsuperscript{−} center in diamond. If $|g_l\rangle$-$|e_l\rangle$ is such a transition, spin in $|e_l\rangle$ can only decay to $|g_l\rangle$, regardless of external magnetic field. Therefore it is trapped in an effective two-level system, as long as there is no optical field exciting spin from $|g_l\rangle$ to $|e_m\rangle$ or $|e_u\rangle$. Spins excited from the other ground states can decay to $|g_l\rangle$ after several excitation cycles, and so the SRA scheme for Π\textsubscript{1} drawn in Fig. 3.2d polarizes spins into the state $|g_l\rangle$ in case of this closed transition. Because after only a few optical excitation cycles there are no spins left in $|g_m\rangle$ or $|g_u\rangle$, the system is insensitive to a second laser addressing those empty states, and hence the associated SRA feature gives no signal. If this closed behaviour gradually disappears beyond 20 mT external field, it might explain the Π\textsubscript{1} SRA feature starting to appear beyond 20 mT in Fig. 3.7a.

This explanation is unsatisfactory, however, when considering what other consequences such a closed transition would have in a measurement of SRA features: it would cause additional SRA features which are not seen in the data. To see this, consider the following, as depicted in Fig. 3.8a. From Fig. 3.7 it is clear that excitation from $|g_l\rangle$ to $|e_m\rangle$ and $|e_u\rangle$ is allowed - otherwise, the Λ\textsubscript{1} and Λ\textsubscript{2} systems A2 and A3 would not be visible. This means that a second laser exciting either of these transitions can remove spins from the bright state $|g_l\rangle$ (green arrow in Fig. 3.8a). After excitation, it can decay to $|g_m\rangle$ or $|g_u\rangle$, which are off-resonant with the lasers. So as a result of the second laser, total absorption would go down. In SRA, this would be visible as features of lower amplitude compared to the single-laser background, i.e. of opposite sign to the features A1-4. These new features would have a splitting equal to $D_e$ at zero field. To show this quantitatively, the full rate equation model described in chapter 2, section 2.8 is solved, with decay from $|e_l\rangle$ restricted to go to $|g_l\rangle$. The result is shown in Fig. 3.8b, showing both features A2 and A3, and the negative SRA features due to the closed transition. Since features of this shape or sign were never observed in our data, a closed transition is not a plausible explanation for the missing Π\textsubscript{1} line.

Intersystem crossing

A second mechanism that could influence the $|g_l\rangle$-$|e_l\rangle$ transition known to exist for divacancies is intersystem crossing (ISC), as described in chapter 2.
Figure 3.8: Possible mechanisms for suppression of the $\Pi_1$ SRA feature A1.  

**a)** Illustration of how a bright, closed transition (orange) can still be emptied by a second laser (green), giving lower total absorption at two-laser resonance.  
**b)** Simulation of the scheme depicted in Fig. 3.8a, with transition $|g_i\rangle-|e_l\rangle$ closed as described in the main text. SRA features of both positive and negative sign result, in places no features are visible in the experimental data in Fig. 3.7a. Also, SRA features of opposite sign would cancel each other when crossing (as seen near 20 mT and 1230 MHz in Fig. 3.8b), which was not observed in experiment.  
**c)** Illustration of how ISC to a metastable singlet state $|s\rangle$ could suppress SRA feature $\Pi_1$.  
**d)** Modelling like in **b)**, but for the scenario with ISC via a metastable singlet state $|s\rangle$ as defined in **c)**, and no closed transition. The suppression of the $\Pi_1$ feature matches the experimental data from Fig. 3.7a, as does the low SRA of all features at magnetic fields below 10 mT. The inset shows the used evolution with magnetic field of the ISC decay rate from $|e_l\rangle$ to $|s\rangle$, as a percentage of the decay rate $G_0$ directly from $|e\rangle$ to $|g\rangle$.  

For ISC, instead of directly decaying from $|e_l\rangle$ to $|g_i\rangle$, the spin can relax to a metastable singlet state, before decaying back to the ground state. This is shown
in Fig. 3.8c, with laser fields coupling the states as for the suppressed Π₁ system A₁. The decay to the singlet state is labeled as $I_j$ for states $|e_j\rangle$. If $I_l$ has a significant value with respect to the direct excited state decay rate $G_0$ (we take $I_l$ up to $0.03G_0$), and $|s\rangle$ has a long lifetime compared to the excited state lifetime $\frac{1}{G_0}$, the spin is optically pumped into the off-resonant state $|s\rangle$. In this way, SRA from the Π₁ system is suppressed. This effect, gradually vanishing towards 70 mT, could explain the suppression of Π₁. Additionally, minor decay from $|e_m\rangle$ and $|e_u\rangle$ to $|s\rangle$ at even smaller magnetic fields would explain the suppression of all SRA features in group A below 10 mT seen in Fig. 3.7a. We also solved the rate equation model for this scenario with ISC. The result is shown in Fig. 3.8d, clearly matching the general behaviour of the lines of group A. In the inset the used evolution of $I_l$ with magnetic field is shown, as a fraction of $G_0$. The other ISC rates $I_m$ and $I_u$ were given the same dependence on magnetic field, but were 100 times smaller than $I + l$.

Forbidden transitions

The last way the Π₁ system could be suppressed, is if the excitation from $|g_l\rangle$ to $|e_l\rangle$ itself remains forbidden, regardless of the mixing of the spin states, and gradually becomes allowed towards 70 mT. Such physics is not captured by the simple spin model used so far. A more complete model that might yield such behaviour is at this point unknown, but could be looked for in the symmetry of the orbital states. Since a magnetic field should make the transition allowed, spin-orbit coupling would also need to be considered, though this is presumed to be small in SiC. Of course, a combination of this effect and ISC could also explain the results.

3.5.5 Identifying group B with magneto-spectroscopy

The SRA features of group A almost completely follow the predictions of a simple model for fully $C_{3v}$ $S = 1$ spin states, as shown in section 3.5.3. Here, it will be argued that although the features from group B probably originate from c-axis divacancies, they can not be explained by a ground and excited state triplet with $C_{3v}$ symmetry.

Fig. 3.9a shows magneto-spectroscopy of predominantly the features belonging to SRA group B, done by setting the carrier frequency $f_C$ to $f_0 + 27$ GHz. The three group B features are labeled as in Fig. 3.5. To try and understand their
Figure 3.9: Magneto-spectroscopy of group A SRA features. a) Probe-laser absorption as measured in Fig. 3.7, for $\varphi = 57^\circ$, now showing predominantly the features from group B due to the high $f_C$. SRA features are labelled as in Fig. 3.5. The black lines are fits to the data (details in main text). b) The same measurement as in a), but with $\varphi$ rotated to $33^\circ$. Black and red lines are fits and model predictions (details in main text). From the shift and shape of feature B1 compared to a, the ground state seems to be an $S = 1$ triplet like the c-axis divacancy ground state, but from the other features, the form of the excited state can not be unequivocally extracted.

origins, only the feature positions will be considered, and no details of optical spin pumping (e.g. their amplitudes). Firstly, feature B1 can be fit perfectly as a $\Lambda$ system formed by $|g_m\rangle$ and $|g_u\rangle$ from an $S = 1$ ground state triplet, using the same $g$-factors and angle as for group A. This fit is shown as the black line overlying feature B1 in Fig. 3.9a. The ground state spin has (at least) two degenerate spin sub-levels at zero magnetic field, since the feature starts at zero detuning at
zero field. An SRA line from a Λ system contains no information on the excited state, and since the line is perfectly straight, it also contains no information on a possible zero-field splitting in the ground state (a robust property from our simulations: no matter the value of $D_g$ in the ground state, at the magic angle the Lambda system between $|g_m\rangle$ and $|g_u\rangle$ is a perfectly straight line). So, from the data in Fig. 3.9a, feature B1 could in principle also be caused by a ground state with spin $S = \frac{1}{2}$. Only a g-factor of $1.87 \pm 0.04$ can be fitted to B1, which is the same value for the features in group A.

Still, evidence that the ground state is (at least) a triplet is obtained from Fig. 3.9b, where the same scan is shown, but with the angle $\varphi$ changed to $33^\circ$. Feature B1 has shifted in response to the new angle between field and c-axis, and also shows a slight curvature. These two changes directly imply an internal quantization axis in the defect, which is a corollary of a zero-field splitting. The black line overlaying line B1 is again the Λ system between $|g_m\rangle$ and $|g_u\rangle$. It matches feature B1 for $D_g = (1.3 \pm 0.2)$ GHz. To illustrate the precision of this fit, model outcomes are shown in dashed red for $D_g = 0.9$ GHz (above) and $D_g = 1.7$ GHz (below), clearly moving away from feature B1. That the ground state can be described by an $S = 1$ triplet with $D_g$ close to 1.3 GHz strongly suggests that group B is still due to c-axis divacancies.

Features B2 and B3 originate from near 720 MHz at 0 mT. Assuming a triplet excited state as well, these two lines cannot be fit with an excited state triplet characterized by only a $D_e$ parameter. For the excited state the Hamiltonian in Eq. 3.2 is needed, including terms associated with the lower $C_{1h}$ symmetry (as also applies to basal plane defects). The best fits, drawn in black in Fig. 3.9a overlaying features B2 and B3, are achieved for $D_e = (940 \pm 20)$ MHz, $E_{x,e} = (-190 \pm 20)$ MHz, and $E_{y,e} = (120 \pm 20)$ MHz. The g-factors were fixed at 1.87, and $D_g$ was fixed at 1.3 GHz, from the fit on feature B1. With this model, feature B2 can only be fit by the transition pair $|g_m\rangle-|e_l\rangle$ and $|g_u\rangle-|e_m\rangle$, and feature B3 only by the pair $|g_m\rangle-|e_m\rangle$ and $|g_u\rangle-|e_l\rangle$. In Fig. 3.7b however, at $\varphi = 33^\circ$, the model wrongly predicts the shifting of feature B2, yet correctly predicts that of feature B3. The prediction for B3 is drawn in solid black, following feature B3 quite well (though feature B3 is not as distinct anymore at this angle $\varphi$). The dashed black line is where the model predicts feature B2 should be, but there is no feature there. In fact, even if all 81 combinations of the 9 transitions between triplet ground and excited state are considered, disregarding the mechanics of SRA, no combination can explain the behaviour of feature B2. A more detailed study of the angle dependence is required: perhaps the unidentified bright feature visible
at low two-laser detuning in Fig. 3.9b is in fact another feature altogether. At this point, however, the exact form of the excited state of group B is still an open question, as is the full character of the defect behind these signals.

3.6 Summary and conclusions

In this chapter, it was shown that the zero-phonon line of PL2 c-axis defect spins is only moderately broadened in an electron-irradiated 4H-SiC sample. This was be done by transmission measurements, giving clear signals in transmission on the order of 1% absorption, due to the high defect concentration compared to as-grown samples. By means of spin-related absorption measurements the homogeneous features of two different spin systems were observed within the ZPL. By spectral hole burning, these were shown to belong to two different physical ensembles of defects. One spin system was shown to consist of an $S = 1$ ground and excited state triplet, consistent with $C_{3v}$ symmetry. The other has a very similar ground state, but an as yet not fully understood triplet excited state. However, by measuring on the low frequency side of the ZPL, at a carefully chosen angle between c-axis and magnetic field $\varphi$ of 57°, homogeneous $\Lambda$ systems from the well-understood first spin system dominate the interaction. This is promising for investigations into optically-driven quantum interference effects in the dynamics of c-axis divacancy spins (see chapter 4).
3.7 Appendix: Polarization dependence

For all the described experiments on divacancy spins oriented along the c-axis, the laser polarizations were linear, and orthogonal to the c-axis. When a laser was polarized along the c-axis, no absorption was observed, and hence the optical dipoles of the spins lie in the basal plane. No increased absorption took place for circularly polarized light: only its projection onto the basal plane was absorbed.

![Graph showing polarization dependence of SRA features.](image)

**Figure 3.10: Polarization dependence of SRA features.** Probe and control beam propagate at (16±1)° from the c-axis. Combinations of orthogonal linear polarizations H and V, written as probe:control in the legend, show that SRA features from groups A and B are strongest for opposite linear polarizations. Magnetic field = 9 mT, temperature = 5 K, \( \varphi = 57° \), \( P_p = 5 \mu W \), \( P_c = 5 \mu W \).

Fig. 3.10 shows how the SRA features depend on the direction of linear polarization. The beams propagate through the sample at (16±1)° from the c-axis. H (horizontal) polarization is along one of the lattice vectors in the basal plane (such as the vector \( P \) in Fig. 2.1 in chapter 2), and V (vertical) is at 90° to H (and thus not along one of the lattice vectors). All four combinations of H and V for the probe and control laser are shown, written as probe:control in the legend. All features from groups A and B described in the main text are indicated by dashed
vertical lines. Though the feature amplitudes only vary by a factor 2 with polarization, the features from group A are strongest for V-polarized light, and those from group B are strongest for H-polarized light, with the mixed polarizations H:V and V:H giving intermediate SRA features amplitudes. These results show that the optical dipoles are non-zero for all directions in the basal plane, but are strongest in one direction, and this direction is opposite for groups A and B. This is expected from theoretical analysis performed on the NV$^-$ center in diamond [50], where a Jahn-Teller distortion causes two stable lattice configurations with optical dipoles oriented at right angles.

3.8 Appendix: Temperature dependence

For SRA features to be visible, the linewidth of individual transitions needs to be narrower than the frequency difference between the transitions. Our experiments show that for divacancies in 4H-SiC, this requires temperature to be only a few Kelvin above absolute zero. As temperature increases, the excited state coherence time decays, and thus the lines broaden.

![Figure 3.11: Temperature dependence of SRA features.](image)

Temperature was varied between 3 and 19 K. SRA features clearly broaden while total SRA lowers for higher temperatures. All SRA features stay centered at the same two-laser detunings (except perhaps feature B1, which seems to shift to higher detuning with increasing temperature, but this is hard to quantify given how strongly it merges with surrounding features). Magnetic field 9 mT, temperature 5 K, $\varphi$ 57°, $P_p$ 5 $\mu$W, $P_c$ 5 $\mu$W.
Fig. 3.11 shows the evolution of SRA features as temperature is increased from 3 to 19 K in steps of 2 K, for PL2 c-axis divacancies. All features broaden, until they are not distinguishable any longer above 11 K. All features seem to stay at the same two-laser detunings as temperature increases, except possible B1, which decays very fast, and/or shifts to higher detuning with increasing temperature. However, this is hard to judge by the broadening and blurring together of the SRA features. The fact that SRA only works well over such a small temperature range makes it an ill-suited method for investigating changes in the behaviour of spins as a function of temperature.

3.9 Appendix: Harmonic SRA overtones

When the setup used in this chapter was changed in several ways, many additional SRA features appeared where none were visible before. Figure 3.12 shows magneto-spectroscopy of both groups A and B, where the probe and control beam are counter-propagating through the sample, the beam probe and control beam diameters are reduced to 20 $\mu$m, both beams propagate close to parallel with the c-axis (at $(16\pm1)\,^\circ$), and the control beam has very high power compared to the probe beam (12 mW and 100 $\mu$W, respectively).

To make the features more clear, a slow-changing background was removed from the figure. The black features are dips, while the bright features are peaks. Features A2 and A3, which are $\Lambda$ systems, show as dips due to electromagnetically induced transparency (EIT) at this high control beam power (see chapter 4 for more on EIT). The harmonics, however, are just as narrow as the EIT features, but are peaks instead of dips. There is a clear symmetry around the features labeled 0', and the features are labelled according to this symmetry, with primes indicating shifted replicas of the already-known features from groups A and B, and stars indicating replicas that are also mirrored. These replicas are because of a coupling of the electronic states to a harmonic oscillator mode, or a direct coupling of the optical field to a harmonic oscillator mode of the entire sample. These harmonic states should have the same zero-field splittings and magnetic-field dependence as the bare electronic states.

The first such harmonic $|g'\rangle$ of the ground state is depicted in Fig. 3.13a, shifted from $|g\rangle$ by 3720 MHz. In the scheme on the left, the origin of the $\Lambda$ system SRA feature A2' is shown. The resulting SRA feature is identical to A2, except its two-laser detuning is shifted up by 3720 MHz. This is caused by
Figure 3.12: Magneto-spectroscopy showing SRA harmonics. When the beams in Fig. 5.1 are made counter-propagating, propagate at (16±1)° from the c-axis, and the beam diameters are reduced to 20 µm inside the sample, more SRA features are visible. These show clear symmetry around the vertical dip at 3720 MHz two-laser detuning, labelled 0', and originate from transitions involving harmonics of either the ground state |g⟩ or excited state |e⟩. Primes indicate the order of the harmonic, stars indicate a mirroring (see Fig. 3.13a). Horizontal lines are artefacts of the measurement, presumably due to small disturbances of the alignment during cryogen refilings. Dis-continuities in SRA harmonics (e.g., the occasional splitting of feature A2') are so-far unknown physics of the harmonics, sensitive to these disturbances. Temperature 5 K, φ 57°, Pp 50 µW, Pc 12 mW.

the high-energy laser coupling to the ground state |g⟩, and the low-energy laser coupling to the harmonic state |g'>. Conversely, when the high-energy laser is coupled to the harmonic state as shown on the right, a mirrored version of feature A2 results, described by 3720 MHz minus the detuning of A2. Subsequent harmonics at multiples of 3720 MHz can also be addressed, and indeed at least two SRA features originating from a second harmonic at 7440 MHz can be seen in Fig. 3.12: A2'" and A3'". The vertical line labelled 0' is a copy of the dip at 0 MHz two-laser detuning, where all transitions are driven by a single laser, removing all SRA. This confirms that indeed the harmonics have the same zero-field splittings and magnetic-field dependence as the phonon-free states. Note that the same shifted and mirrored copies of SRA features would result if the excited state has harmonic states: from which state the harmonics originate is at this point unknown.
3.9 Appendix: Harmonic SRA overtones

Figure 3.13: Model and control beam power dependence of SRA harmonics.

a) The triplet ground and excited state model from Fig. 3.2d, with a harmonic of $|g'\rangle$, 3720 MHz above $|g\rangle$. Left is the Λ SRA feature A2': the laser of lower energy (orange) couples the harmonic $|g_m'\rangle$ to $|e_m\rangle$. A2' thus evolves with magnetic field identically to feature A2, but with two-laser detuning increased by 3720 MHz. Shown right is the feature A2'*: the laser of higher energy (green) couples the harmonic $|g_l'\rangle$ to $|e_m\rangle$. A2'* thus evolves with magnetic field as 3720 MHz minus A2 (so mirrored from A2).

b) SRA features with control beam powers of 20 μW, 500 μW, and 14 mW, and probe beam power of 100 μW. As the control power increases, the non-harmonic SRA features (B1-B2 and A1-A3) show power broadening, and A2 and A3 show EIT dips at 14 mW control power. The first-order harmonics (single prime) show relatively little power broadening, and the second-order harmonics (double prime) are only visible for the highest control power. Magnetic field = 40 mT, $\varphi$ = 57°, temperature = 5 K.

During the taking of this dataset, cryogens had to be refilled several times, resulting in slight discontinuities in the dataset, seen as horizontal lines in the plot. This is presumably due to small changes in alignment due to handling of the cryostat. Though not visibly affecting the original features from group A and B, several harmonics change quite drastically: they vanish, become stronger, or even change shape. This can be most clearly seen in features 0', A2''* and A2', which sometimes consist of two separate lines, and then suddenly of one line again. Due to this unstable behaviour, it was not possible to unambiguously find which change in the setup caused the harmonics so appear, though it was observed the harmonics faded somewhat when the beam diameter was increased to 70 μW, and disappeared when the beams were made to co-propagate. Also of
note, is that the feature 0’ was seen to slightly shift between different spots on the sample, by up to 20 MHz.

In Fig. 3.13b, the control beam power dependence of the SRA features and their harmonics is shown, at a magnetic field of 40 mT. The control beam was set to 20 $\mu$W, 500 $\mu$W and 14 mW, while the probe beam was kept at 100 $\mu$W. Dashed lines indicate the SRA features. The features B1-B2 and A1-A3 (the non-harmonics) are power broadened to three times their width between the lower two powers, and are several GHz wide at 14 mW control power. The A systems A2 and A3 show EIT for the highest control power. On the other hand, the first-order harmonics (single prime) barely change width over three orders of magnitude of control beam power, which is at this point not understood. The second order harmonics (double prime) are only visible for the highest control power.

### 3.10 Appendix: Magneto-spectroscopy of PL1

Lower in energy from the ZPL of PL2 by 380 GHz lies the ZPL of PL1, the second distinct c-axis divacancy in 4H-SiC, as seen in the inset of Fig. 3.1. In Fig. 3.14, the result of magneto-spectroscopy as in sections 3.5.3 and 3.5.5 is shown, with the lasers now tuned to the center of the PL1 ZPL. Temperature is 4.2 K, $\varphi = 33^\circ$ (so away from the magic angle). The measurement was performed on the same sample as with the PL2 measurements.

![Figure 3.14: Magneto-spectroscopy of the PL1 c-axis divacancy spin. The same features as in Fig. 3.7 and 3.9 for PL2 are visible. Apparently, the physics of SRA is largely the same for the PL1 divacancy spin. The only significant difference is a splitting of (400±20) MHz at zero magnetic field between features B2 and B3.](image-url)
The SRA features in Fig. 3.14 are nearly identical to those found for PL2. The features have been labelled in the same way as was done in Fig. 3.7 and Fig. 3.9. Since the carrier frequency is set to the center of the ZPL, groups A and B are visible simultaneously. One apparent difference from the SRA of PL2 is that features B2 and B3 seem to be significantly split apart at zero magnetic field, by (400±20) MHz.