Two-laser spectroscopy and coherent manipulation of color-center spin ensembles in silicon carbide
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Chapter 5

Exploring the spin structure of the Molybdenum impurity in 4H-SiC

Abstract
Molybdenum impurities in several SiC polytypes have previously been reported to host $S = 1$ spins, which should be directly optically addressable. Analogously to the well-known NV$^-$ center in diamond, as well as several more recently investigated defects in wide-bandgap semiconductors, its energy levels are deep in the semiconductor gap. If the spin coherence time is much longer than the excited state lifetime, it is an interesting candidate system for all-optical quantum information applications. This chapter describes the all-optical probing of the ground and excited spin states, and the transitions between them, of an ensemble of Mo impurities in 4H-SiC. From photoluminescence (PL) and PL excitation (PLE) with a single laser, the transitions are found to be inhomogeneously broadened. It is then argued that optical spin pumping takes place in Mo defect spins in 4H-SiC. By varying the detuning of a second laser as well as a static magnetic field, homogeneous signatures of the underlying spin states are recovered in PLE. These features show that the magnetic field does not mix the spin states in either ground or excited state, implying there are no zero-field splittings in the probed ensemble, contrary to what has been reported in literature. The observed dependence on external magnetic field orientation can, however, be well described by anisotropic g-tensors. Also, a sharp feature reminiscent of coherent population trapping is observed, which gradually vanishes between 4 and 10 K.
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5.1 Introduction

One can never grow a perfectly pure crystal: lattice defects and trace impurities are inevitable in any realistic growth procedure due to basic thermodynamics, and the fact that the growth apparatus itself will dope the crystal during growth. For semiconductors, many such point defects form deep levels in the bandgap. These can be stable for several charge states, acting as long-lived charge traps, hindring device performance when charges are supposed to flow. Intentionally adding doping during growth can counter this effect to create net trap-free crystals, or one can dope orders of magnitude more to create p- or n-type doped crystals [59] [60]. For silicon carbide, particularly the 4H and 6H polytypes, this is now established practice in industry, and crystals doped with vacancies and conventional dopants are commercially available.

Besides this established defect functionality, such defects have recently come into focus as promising candidates for quantum information science. In diamond, the NV\(^{-}\) center has pioneered the field of quantum optics with color centers [9]. More recently, other defects, both in diamond and in other wide-bandgap semiconductors, have also started attracting attention [58] [37] [36] [39]. An interesting example in diamond is the silicon-vacancy center, which has orders of magnitude less phonon-assisted decay between excited state and ground state than NV\(^{-}\) centers [61], a key property for scalable applications. Initially in SiC, divacancies were shown to have long-coherent spins, all the way up to room temperature [10] [21]. Various other defects in SiC, both as ensembles [11] [48] [57] and single defects [22], were then shown to be viable candidates for quantum information science. Looking to further explore possible qubits in SiC, transition metal dopants such as molybdenum and vanadium look promising from theoretical investigations and early electron spin resonance (ESR) and photoluminescence (PL) studies [15] [62] [63]. For Mo, these studies conclude that Mo is stable in several charge states, of which the double-positively charged form is directly optically accessible [64]. The spin of this charge state was reported to be \(S = 1\), with a zero-field splitting of 3-6 GHz in the ground state. It was predicted that Mo prefers to occupy divacancy sites where both vacancies are in a hexagonal crystal environment (hh-symmetry), which only occurs along the crystal growth axis (c-axis) [14]. The number of Mo zero-phonon lines (ZPL) in different SiC polytypes was seen to equal the number of hh-divacancies in the crystal. Dubbed the asymmetric split vacancy (ASV) configuration (due to Mo not being exactly in the divacancy center), the system has \(C_{3V}\) symmetry, with the zero-field split-
ting quantization axis along the c-axis. An ensemble of Mo defects is hence mono-directional, which could be beneficial when designing actual devices. These properties would be favourable for all-optical quantum information applications and motivated the research presented in this chapter: to all-optically investigate the yet-unknown lifetime and coherence properties of the Mo spin ground state and its excited state, and the transitions between these states.

In this chapter, results are presented first on single-laser spectroscopy performed on an ensemble of Mo impurities in 4H-SiC, revealing an inhomogeneous broadening of the spacing between ground and excited state. Next, from two-laser experiments, evidence for optical spin pumping (OSP) in Mo impurities is given. This allows for investigation of the spin sub-levels in ground and excited state by means of spin-related emission (SRE) spectroscopy, as described in chapter 1. The homogeneous features thus recovered shift linearly with magnetic field strengths up to (at least) 1.2 T. It is argued that this implies that all ground state spin levels are degenerate at zero field. Additionally, a strong dependence on the orientation of an external magnetic field is observed: the apparent g-factor characterizing how strongly levels shift with magnetic field, the number of observed features, and the presence of sharper sub-features resembling coherent population trapping (CPT), all depend on the angle between the c-axis and the direction of the applied magnetic field. This is shown to be consistent with anisotropic g-tensors. The data thus contradicts the notion of $S = 1$ spin triplets with non-degenerate spin sublevels at zero magnetic field (zero-field splittings) for Mo impurities in 4H-SiC reported in [15].

## 5.2 Experiment

The sample used was p-type, doped with Mo. The doping concentration was estimated to be between $10^{15}$ and $10^{17}$ cm$^{-3}$, judging from comparison of its photoluminescence spectra with those of a sample of $10^{15}$ cm$^{-3}$ (as measured by secondary ion mass spectrometer). The sample was the same as that used in [62], where it was concluded based on the polarization of the emitted photoluminescence (PL) that the most likely charge state of the defects is double-positively charged. Due to background absorption of unknown origin, the sample was highly absorbing over a wide wavelength range in the infrared, making it impossible to look for Mo signatures in transmission. All results presented here therefore come from PL or PL excitation (PLE) measurements, performed on a corner of the sample, so as to minimize decay of the lasers and emitted light inside the sample.
material.

Figure 5.1: Experiment schematic. Excitation lasers (red) overlap in the sample (gray), exciting Mo impurities (bright blue). The lasers (parallel to each other within 3° within the sample) are aligned on the sample edge. This allows the subsequent emission of Mo to exit the sample after only very short propagation through the material, minimizing re-absorption. An NA = 0.5 lens mounted 1 cm from the sample inside the cryostat collimates the emitted light, which is passed to a spectrometer or single-photon counter. The sample was mounted at various angles $\phi$, the angle between applied static magnetic field and the SiC c-axis. A 770 nm laser (drawn in orange) prevents the defects from permanently switching to another charge state.

As shown in Fig. 5.1, excitation lasers were focussed to a 70 µm spot at the edge of the sample, and light exiting the nearby side of the sample was collected with a high-NA lens. For PL, the light was brought to an Ocean Optics NIRQuest spectrometer with 3 nm resolution, while for PLE the total PL was measured by an InGaAs single-photon counter. The sample temperature was varied between 4 and 20 K in a helium flow cryostat, and a static magnetic field could be applied at various angles $\varphi$ with respect to the material’s c-axis. It is also important to note that at all times during these experiments, a 40 µW pulsed 770 nm laser (~200 ps pulses, 80 MHz repetition rate) was focussed on the defects, to rapidly return Mo impurities to the required charge state after a bleaching event [43] (see 2, section 2.11 for a description of this phenomenon in basal-plane divacancies in 4H-SiC - the Mo impurities seems to behave quite similarly). All lasers are parallel to within 3° inside the sample.
5.3 Single laser spectroscopy results

As a starting point for optically studying Mo impurities in SiC, their photoluminescence is shown in Fig. 5.2, for several temperatures. The excitation source was [waiting for reply collaborator]. Earlier work identified the sharp feature just above 1.15 eV as the ZPL of the defect, which is the signal of direct transitions between the ground and excited states. The other peaks at lower energies have all been identified in earlier work to be phonon replicas of the ZPL. This is very much like the phonon sidebands (PSB) seen in previous chapters on divacancies in SiC, with the difference that the divacancy PSB appears as many closely spaced phonon replicas, combining into a continuous band.

Figure 5.2: Molybdenum impurity photoluminescence. PL from excitation with a 514.5 nm laser, detected with an FTIR spectrometer, for sample temperatures between 5 and 20 K. The Mo ZPL is at 1.1521 eV, and the broadener peaks at lower energies are phonon replicas of the ZPL. There is almost no dependence on temperature in both ZPL and replicas. The inset shows a close-up of the ZPL for the same temperature range. Data courtesy of A. Gällström, Department of Physics, Chemistry and Biology, Linkping University, Sweden.

Since there are four inequivalent divacancies in 4H-SiC, and Mo impurities were originally predicted to occupy the silicon position in divacancy sites, one might expect four distinct ZPL’s from Mo impurities, as there are four such lines for divacancies themselves (see chapters 3 and 2). However, there is only one Mo ZPL visible, consistent with Mo only occupying hh-divacancies along the c-axis, of which there is only one in 4H-SiC.
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Figure 5.3: Inhomogeneous Mo impurity ZPL measured by PLE. The PLE signal is the integrated phonon replica emission, in response to a single CW narrow-linewidth laser scanned over the ZPL, for temperatures between 4 and 20 K. When the temperature is lowered, the width of the ZPL stays roughly the same, but the height drops significantly. Combined with the near-independence of temperature of the ZPL and phonon replica emission seen in Fig. 5.2, this is a strong indication for optical spin pumping in Mo divacancies at lower temperatures. The peak position is shifted with 0.2 meV compared to Fig. 5.2, which is within the uncertainty of [waiting for reply collaborator]. Experiments with laser resonant with the ZPL were performed within 0.1 meV from the ZPL peak.

Fig. 5.3 shows PL excitation (PLE) traces of the Mo impurity ZPL, obtained by scanning a CW narrow-linewidth laser over the ZPL, and collecting the phonon replica emission, again for several temperatures. While this high-resolution method could show the homogeneous fine-structure transitions between ground and excited state, instead a broadened line of \((23 \pm 1)\) GHz \([(0.90 \pm 0.05)\) meV] is seen. This inhomogeneous broadening masks the homogeneous spin levels and transitions, as was the case in chapters 3 and 2 on divacancies. As long as it is mostly a broadening of the transition energy from ground to excited state, and not a broadening of the spin levels within those states, the homogeneous features can be recovered by spin related emission (SRE) spectroscopy, as described in detail in chapter 1.
5.4 Two-laser spectroscopy results

5.4.1 Characterization of the homogeneous linewidth

A requirement for SRE is optical spin pumping when resonance occurs with a single CW laser at low enough temperature. This laser excites spin from a ground state level, after which the spin decays to one or more off-resonant, long-lived levels or states (e.g. other ground state spin sub-levels, metastable states of different total spin, or other charge states). For instance, the lifetime of the ground state spin sub-levels is typically very long compared to the excited state lifetime in deep defects, which would cause that the spin is not interacting with the laser for most of time in such an experiment.

A first indication that this indeed happens for Mo defects can be seen in the PLE temperature dependence in Fig. 5.3. Lowering the temperature from 20 to 4 K, the ZPL measured with PLE strongly decays (in addition to a small shift to lower energy). While this could be explained by less emission into the phonon replicas for lower temperatures (the detection channel for PLE), Fig. 5.2 shows that over this temperature range the phonon sideband emission is almost temperature-independent (which has been observed to hold to within a factor 2, all the way up to room temperature [62]). This means that the lowering of the ZPL is due to a decrease in interaction with the laser resonant with the ZPL, a strong indication of optical spin pumping.

For a first indication of the homogeneous linewidths of the Mo transitions, the non-linear response to the laser intensity of SRE can be used. To see this, consider the following: when a laser is polarizing spin into an off-resonant state, the amount of light absorbed by the impurity is mainly governed by the lifetimes of the spin states, and not the laser power. Simply put, for high enough power the system is saturated. Doubling the laser power therefore leads to less than double emission into the phonon replicas. When two equal-power lasers are resonant with the inhomogeneous ZPL, but far enough detuned from each other so as not to address the same spins, the total absorption is the sum of both lasers’ absorption, so double that of a single laser. When the detuning is reduced to within the homogeneous linewidth of the transitions, effectively the experiment changes to a single laser of twice the power, addressing half as many defects. Due to the saturation, this gives less total absorption. The results of such a measurement, for temperatures between 4 and 8 K, are shown in Fig. 5.4.

Both laser beams had 7 $\mu$W power, focussed down to a 70 $\mu$m diameter spot. In these scans for detunings below 100 MHz the PLE could not be observed, due
Figure 5.4: Saturation spectroscopy of homogeneous linewidth. PLE from two lasers tuned to the center of the inhomogeneously broadened ZPL peak, as a function of the detuning of the lasers, for temperatures between 4 and 8 K (traces not offset, 0 mT). The traces show a dip at zero detuning for all temperatures, a strong indication of optical spin pumping. The inset shows the FWHM of a Lorentzian fit to the dips, showing clear broadening towards higher temperature. This indicates a strongly decreasing excited state lifetime, consistent with optical spin pumping.

It is worth noting that in principle, any saturation with power would yield such PLE dips at zero detunings. For example, when strongly driving a two-level system population saturates to a 50-50 distribution between the two states, which yields a certain emission. In this situation, two far-detuned lasers addressing separate two-level systems cause more emission than when both lasers are
pumping on the same, already saturated system. So on their own, these dips are not unequivocal proof of OSP, or the existence of a ground state with two or three spin sub-levels - they just prove saturation. However, combined with the overall lowering of the ZPL discussed in the previous section, the fact that the ground state is expected to be a spin multiplet with long-lived sublevels, and the intensity of the lasers being quite low for directly saturating transitions (for comparison, with divacancies in 4H-SiC, 1000 times more power than used here does not even start to saturate transitions), it is plausible to ascribe this behaviour to OSP. Care is required though: the linewidth of these dips does not guarantee all the spin transitions will have this linewidth. Different excited state levels might still have different linewidths, e.g. due to spin-dependent indirect decay mechanisms like intersystem crossing. Not all transitions are being driven by the lasers applied here (if they were, there would be no spin polarization), and hence this dip does not necessarily represent all transitions the spin might make. It does, however, provide a useful first estimate of the width of features to look for in SRE magneto-spectroscopy.

5.4.2 Spin-related emission magneto-spectroscopy

Figure 5.5a shows PLE as a function of two-laser detuning and magnetic field. The angle $\varphi$ between the static magnetic field and the c-axis was set to 32°, and the temperature was set to 4.2 K. A single SRE feature is visible, linear in magnetic field, labelled A1. The feature is relatively weak, less than 5% of the background PLE. In comparison: for basal plane divacancies the SRE features could be up to 100x larger than the background PLE in a similar experiment. In Fig. 5.5b a similar result is shown, where the angle $\varphi$ was rotated to 57°. Three straight SRE features are visible, shifting away from 0 MHz at zero external magnetic field, labelled B1, B2 and B3 with increasing slope $S = \frac{dB}{d\delta}$ (where $B$ is magnetic field strength, and $\delta$ is the two-laser detuning). Remarkably different from magneto-spectroscopy on divacancies in previous chapters, SRE features of both positive and negative sign are visible. The feature A1 from Fig. 5.5a is gone at this angle $\varphi$, or has shifted, indicating a dependence of SRE on magnetic field orientation. In Fig. 5.5c a third similar result is shown, where the angle $\varphi$ was rotated further to 87°, the temperature was 10 K, and both magnetic field and detuning were scanned to higher values than before. Again there are SRE features starting at 0 MHz and 0 mT, labelled C1-4. Clearly, the SRE features depend on $\varphi$, since again the number of features, and the slopes of these features
Figure 5.5: Spin-related emission features in magneto-PLE. a) PLE as a function of two-laser detuning and static magnetic field strength, with the field at 32° from the c-axis, and temperature at 4.2 K. One clear linear SRE feature is visible. In red is drawn the line $\delta = g\mu_B B / h$ with $g = 2$, implying the actual g-factors must be much smaller than 2. b) Measurement result as in a), for $\varphi = 57^\circ$. Three linear SRE features are now visible, labelled B1-3, where B1 and B3 show higher PLE than the background, and B2 shows lower PLE. The decay of the PLE background towards lower detunings is the saturation spectroscopy dip seen in Fig. 5.4. The features B1-3 are clearly several times narrower than this saturation dip, and originate at 0 MHz and 0 mT. c) Measurement result as in a) and b), except over a larger range of detuning and field, with $\varphi$ rotated to 87°, and temperature set to 10 K. At these settings, there are four clear SRE features, labelled C1-4, all with lower PLE than the background. Again, all features start at 0 MHz, and are linear with magnetic field. The plot has the same aspect ratio as a) and b).
are different between $\varphi = 87^\circ$ and $\varphi = 57^\circ$. That the slopes are not identical can be evaluated directly from these plots, since figures 5.5a-c have the same aspect ratio.

In chapters 2 and 3, the existence of spin $S = 1$ ground and excited states with zero-field splittings was directly deduced from the SRE features. The key properties for this were that they originated at non-zero two-laser detunings at 0 mT, and their non-linear shifting with magnetic field due to mixing of the spin sublevels. However, all features observed in Fig. 5.5a-c originate at 0 MHz, and are perfectly linear with magnetic field. It will be argued in section 5.5.1 that this conflicts with the notion of zero-field splittings in both ground and excited state. Also, the features shift very slowly with magnetic field. For reference in Fig. 5.5a-c, a red dashed line indicating $\delta = g\mu_B B/h$ is drawn, where $g$ is the g-factor set to 2, $\mu_B$ is the Bohr magneton, $B$ the magnetic field strength, and $h$ Planck’s constant. By measuring on a sample with a high divacancy concentration, in the same measurement volume as the Mo-rich sample, the magnetic field strength was confirmed to be accurate, leaving a g-factor smaller than 2 to explain the slow shifting. This is also further explored in section 5.5.1.

### 5.4.3 CPT-like sharp SRE features

For a further study of the sign of the spectral features, Fig. 5.6a shows a close-up of line B1 at 4.2 K and 100 mT, for different applied laser powers. The SRA feature is actually a 200 MHz broad dip, with a sharper 70 MHz wide peak in its center, highlighted in grey. This narrower width of the center peak is reminiscent of coherent population trapping (CPT, see chapter 1), where the feature width is set by the ground state coherence time, which is much longer than the excited state lifetime. Also, the opposite sign of the CPT-like feature compared to the sign of the the broader surrounding feature is to be expected for CPT. If the broader feature is due to several transitions being driven simultaneously, and CPT effectively stops some of those transitions due to quantum interference in the excitation dynamics, the total PLE will be closer to the background PLE again.

However, a CPT peak originating from a $\Lambda$ system would be expected to depend strongly on laser intensity. When the intensity of both lasers goes down, and driving of the transition is slower than the ground state dephasing time, CPT should vanish. When the intensity goes up, the CPT feature should broaden, eventually splitting the broader feature into two peaks (Autler-Townes splitting).
Figure 5.6: Intensity and temperature dependence of sharp counter-features. a) PLE of SRE feature B1 at 4.2 K and 100 mT, for several laser intensities (both lasers equal). An additional repump laser of equal power is present to prevent optical bleaching. Each trace is normalized to 1, and they are vertically offset for clarity. For all intensities, a broad 200 MHz FWHM dip is visible, with a sharper 70 MHz FWHM peak in its center (highlighted in grey). Due to its narrow width compared to the broader dip, and the opposite sign to the dip, this counter-feature resembles CPT, yet it does not vanish for lower intensity. b) Close-up of SRE features C2 and C3 at 100 mT, 500 µW laser powers, for temperatures between 4 and 8 K. The counter-feature peak at 3160 MHz detuning (highlighted in grey) vanishes with increasing temperature, and only the surrounding broader dip is visible at 8 K. The broader dip at 2800 MHz stays the same.

Fig. 5.6a shows that, if anything, the narrow peak gets more pronounced for 250x lower laser intensity, compared to both the total PLE and the broader dip surrounding the counter-feature. Speculating, this might mean that the CPT is not taking place in a Λ system where two ground states are coupled to the same excited state, but in a V system, coupling one ground state to two excited states.
In such a laser configuration, additional effects such as saturation of transitions plays a role, and the power dependence becomes more complicated [66]. From here on, these features (that may or may not be CPT) will be called counter-features.

Regardless of the Λ, V, or other type of system that might underly the counter-features, if they come from a quantum interference effect, they are sensitive to the coherence times of the states involved. Coherence times might in turn decay with increasing temperature. Figure 5.6b shows a scan over features C2 and C3 at temperatures between 4 and 8 K, showing a counter-feature in C3 (high detuning). In this temperature range, C3 has a counter-feature that disappears with increasing temperature (and presumably decreasing coherence) supporting that they are due to quantum interference effects in the excitation dynamics. Feature C2, meanwhile, stays unchanged. Repeating this measurement for all features shown in Fig. 5.5, B1, B3 and C3 are found to have counter-features.

5.5 Analysis

5.5.1 Modelling the line positions

To first explain only the spectral positions of SRE features in magneto-spectroscopy, ignoring the details of optical spin pumping (i.e. amplitude, sign, and linewidth), it helps to explicitly write down the equations for completely straight SRE features as seen in Fig. 5.5. The Hamiltonian for a spin in a crystal with $C_{3V}$ symmetry can be written as

$$H_{g(e)} = g_{g(e)}\mu_B \vec{B} \cdot \vec{S} + hD_{g(e)}S_z^2,$$

where $g_{g(e)}$ is the g-factor in the ground (excited) state, $\mu_B$ the Bohr magneton, $\vec{B}$ the static external field, $h$ is Planck’s constant, $D_{g(e)}$ is the splitting between the $m_s = 0$ and the $m_s \neq 0$ sub-levels due to spin-spin interaction in the ground (excited) state, and $\vec{S}$ the unitless Pauli spin vector. For SRA features to originate at 0 MHz two-laser detuning, the involved energy levels in ground and excited state need to be degenerate at zero field, i.e. $D_{g(e)} = 0$. The Hamiltonian of such a spin state is just the Zeeman Hamiltonian

$$H = g_{g(e)}\mu_B \vec{B} \cdot \vec{S},$$

(5.2)
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Note that this equation is valid for any spin quantum number of the state. The eigenenergy $E_i$ for ground state $|g_i\rangle$ or excited state $|e_i\rangle$ obtained from this Hamiltonian shifts from its initial value with $B = |\vec{B}|$ according to

$$\Delta E_i = g_{g(e)} \mu_B B m_i,$$

where $m_i$ is the quantum number for the spin component along $\vec{B}$. The frequency $f_{ij}$ of a transition between a ground state level $|g_i\rangle$ and excited state level $|e_j\rangle$ then changes with $B$ as

$$\Delta f_{ij} = \Delta E_j - \Delta E_i = g_e \mu_B B m_j - g_g \mu_B B m_i = \mu_B (g_e m_j - g_g m_i).$$

Finally, the frequency of SRE features $\sigma_{ijkl}$ are the absolute value of the differences between a pair of transition frequencies. Taking transitions between $|g_i\rangle$ and $|e_j\rangle$, and between $|g_k\rangle$ and $|e_l\rangle$, SRE features thus change with magnetic field as

$$\sigma_{ijkl} = |\Delta f_{ij} - \Delta f_{kl}| = |\mu_B (g_e m_j - g_g m_i) - \mu_B (g_e m_k - g_g m_l)| = \mu_B |g_e \Delta m_{ji} + g_g \Delta m_{kl}|.$$

where $\Delta m_{ki(jl)}$ is the quantum number difference of the involved ground (excited) states. From Eq. 5.5, it can be seen that the linear SRE features $\sigma_{ijkl}$ of a state with some $S = n$ are a subset of the features of a state with $S > n$. An increase in $S$ allows larger spin differences $\Delta m_{ki(jl)}$, and hence additional $\sigma_{ijkl}$ that shift more strongly with magnetic field.

To explain the positions (and only positions) of up to four spectral lines, which is the maximum number seen for Mo in Fig. 5.5a-c, only two levels in both ground and excited state are in principle required. Such an $S = \frac{1}{2}$ system is depicted in the blue boxes in Fig. 5.7a. If those are the only spin energy levels, $\Delta m_{g(e)}$ can be -1, 0 or +1, and hence $\sigma_{ijkl}$ can be $\mu_B B g_g$, $\mu_B B g_e$, $\mu_B B (g_e + g_g)$ or $\mu_B B |g_e - g_g|$. Allowing the g-factors to vary, these lines can be used to fit the SRE features in Fig. 5.5a, b or c, but not at the same time: the SRE features
5.5 Analysis

![Diagram showing fine structure models and data fitting](image)

**Figure 5.7: Fine structure models underlying observed SRE features.**

a) In the blue boxes, spin doublets in ground and excited state are drawn, degenerate at zero field. They split as the magnetic field strength increases, non-parallel with the z-axis of the defect. Outside the blue boxes third levels are drawn, split off by zero-field splittings. Towards higher magnetic field, where the Zeeman shift is on the order of the zero-field splitting, these extra levels cause avoided crossings. Such bending is not observed in the data for reasonable $D_g$ and $D_e$. b) The solid lines are fits of Eq. 5.5 to the data: green for $\varphi = 87^\circ$, black for $\varphi = 57^\circ$, and red for $\varphi = 87^\circ$. The dashed green lines are typical outcomes of Eq. 5.1 with a third level causing avoided crossings. The fit parameters found for C1-C4 are used, together with $D_g = 5$ GHz and $D_e = 3$ GHz. The lines are no longer linear due to the zero-field splittings.

were found to depend on the angle $\varphi$ between c-axis and magnetic field, and such a dependence is not covered by Eq. 5.5.

To have the model account for the observed dependence on magnetic field orientation, $g_g$ and $g_e$ have to be anisotropic, with a particular value parallel to the c-axis, and another perpendicular to it for the most general case ($g$ is a tensor). This causes Eq. 5.5 to expand to

$$\sigma_{ijkl} = \mu_B B \sqrt{(g_g^\parallel \cos \varphi)^2 + (g_g^\perp \sin \varphi)^2 \Delta m_{ki} + (g_e^\parallel \cos \varphi)^2 + (g_e^\perp \sin \varphi)^2 \Delta m_{jl}}.$$  \hspace{1cm} (5.6)

Fitting Eq. 5.6 for two $S = \frac{1}{2}$ systems to the SRE features at $\varphi = (32 \pm 1)^\circ$, 
(57 ± 1°) and 87 ± 1° at the same time, values of $g || = 2.0 ± 0.1$, $g ^ \perp = 0.17 ± 0.02$, $g || = 0.48 ± 0.02$ and $g ^ \perp = 0.23 ± 0.02$ are found to give good agreement between the model and all observed features, with $\sigma_{ijkl}$ falling within all the homogeneous linewidths (fits shown as solid lines in Fig. 5.7b). Explaining why all four $\sigma_{ijkl}$ are not visible for all $\phi$ would require a more complete analysis, taking into account optical spin pumping, and is beyond the scope of this chapter. With this fit, all SRE features that show counter-features are identified as $\Lambda$ ($V$) systems, where the lasers address the same ground (excited) state and quantum interference in the driven dynamics is a possibility. For all features with no counter-feature, except for C2, all four spin sub-levels are involved, which indeed does not allow for quantum interference. It is possible for a $\Lambda$ or $V$ system to not show CPT (for instance due to more spin-sublevels being involved). So, no counterfeature in C2 does not disprove quantum interference being responsible for the counter-features (seeing a counter-feature in a $\Pi$ system, with all four levels involved, would disprove it). Hence we conclude that quantum interference could very well be the reason behind the counter-features.

An important note about these fits: so far no assumptions have been made about the details of optical spin pumping, or about the roles of the two lasers in creating SRE features. In other words: since only frequency differences matter, the ground and excited state are interchangeable for the fits of $\sigma_{ijkl}$ to work. Either way, these values are quite far from those reported in literature [15], where an isotropic g-factor close to 2 was found for the ground state. The reason behind this discrepancy is at this point unknown.

While the positions of the lines can be explained with an $S = \frac{1}{2}$ model for ground and excited state, when also considering their amplitude and sign, an additional metastable state is required. This is discussed in the next section.

5.5.2 Optical spin pumping: an additional metastable state

When considering the SRE feature amplitudes, and specifically their sign (as well as earlier literature on Mo in 4H-SiC), two ground state sub-levels are not sufficient. Since several SRE features show less PLE than the background, the spins must be pumped into some off-resonant, long-lived state. Since Mo was previously reported to have an $S = 1$ ground and excited state, a third spin sub-level is the candidate analyzed here first. If all three levels are degenerate at zero magnetic field, the line positions are still described by Eq. 5.5, and the analysis in the previous section remains valid. For an $S = 1$ ground and excited state,
there are 12 distinct $\sigma_{ijkl}$, 8 more than for $S = \frac{1}{2}$, and these 8 are expected to shift more strongly with magnetic field. These features are not seen in Fig. 5.5 for any angle $\varphi$. Though the absence of these lines does not support $S = 1$, it also does not disprove a third level: to explain which SRE features are visible in PLE a more complete model is required, that includes the dynamics of optical spin pumping (see chapter 2), which is beyond the scope of this chapter.

If, however, there are zero-field splittings present, as has been predicted from theory for these defects, that would expand the model system all six levels in Fig. 5.7a, with levels with $m_s \neq 0$ split off by $D_g$ and $D_e$. The main problem with this scenario is that for $D_g$ and $D_e$ of a reasonable size (within the width of the inhomogeneously broadened ZPL) non-linear shifting of the SRE features with magnetic field is expected due to spin mixing. This non-linearity can be understood as a gradual change of the spin quantization axis $\hat{z}$, with $\hat{z}$ first pointing along the built-in quantization axis (typically along the c-axis for $C_{3V}$ symmetry), and then gradually aligning fully along $\vec{B}$ as $B$ increases. When the external magnetic field is on the order of the zero-field splittings, the spin states are mixed, and the energy levels bend (this is the same physics underlying the dependence of electron paramagnetic resonance (EPR) signals on static magnetic field orientation [63]). A hypothetical representation of such bending of the levels is depicted in Fig. 5.7a, calculated from Eq. 5.1. In Fig. 5.7b the effect of this bending on SRE features is shown, for $\varphi = 87^\circ$. The solid lines are the fits to the peak positions in Fig. 5.5a-c, whereas the dashed lines are the predicted $S = 1$ SRE features for $D_g = 5$ GHz and $D_e = 3$ GHz. Clearly, Eq. 5.1 with $S = 1$ and zero-field splittings cannot describe the observed features.

If due to strong spin-orbit coupling the system must be described by a more comprehensive Hamiltonian with additional orbital degrees of freedom, where the avoided crossings become normal crossings, the $S = 1$ scenario could still hold. In that case, the spin would have a fixed quantization axis, presumably the c-axis due to the $C_{3V}$ symmetry, which is not significantly perturbed by a magnetic field. In this scenario, the magnetic field in Eq. 5.5 is replaced by the projection of $\vec{B}$ on this fixed axis, so $B \rightarrow B \cos \varphi$, and hence SRE features are described by

$$
\sigma_{ijkl} = \mu_B |g_g \Delta m_{ki} + g_e \Delta m_{jl}| B \cos \varphi.
$$

Due to this projection of $B$ along $\hat{c}$, only the g-factor components $g^\parallel_g$ and $g^\parallel_e$ can influence the SRE features. However, fitting to all three angles $\varphi$ in Fig. 5.5...
simultaneously with this built-in quantization axis model turns out to be impossible, when fitting \( g \| \) and \( g \perp \). The best fit to \( \varphi = 87^\circ \) yields \( g \| = 0.95 \) and \( g \perp = 0.85 \), whereas for \( \varphi = 57^\circ \), \( g \| = 0.66 \) and \( g \perp = 0.28 \). This makes the scenario of \( S = 1 \) with zero-field splittings further unlikely. It also leaves unanswered the question what the metastable state responsible for SRE in section 5.4.1 is, if not a third split-off ground state spin sub-level.

5.6 Summary and conclusions

In this chapter the ZPL of Mo impurities in a p-type 4H-SiC sample was shown to be inhomogeneously broadened, from which homogeneous spin signatures could be extracted by exploiting optical spin pumping. Using two precisely detuned lasers, a static external magnetic field, and an additional repump laser to prevent Mo defects from switching charge state, spin-related emission features became visible below 10 K. These homogeneous magneto-spectroscopy lines are perfectly linear with magnetic field up to (at least) 1.2 T, which conflicts with previous EPR studies claiming \( S = 1 \) spins with zero-field splittings on the order of 4 GHz for the ground and excited states. To explain the line positions in magneto-spectroscopy, only a (sub-)system of two \( S = \frac{1}{2} \) spins is required, degenerate at zero magnetic field. To also explain the sign of the lines (a lowering of the PLE), an additional metastable state is required. If this is a third ground state level, and hence \( S > \frac{1}{2} \), it has to be degenerate at zero magnetic field as well, since there are no avoided crossings, as seen in magneto-spectroscopy. The features strongly depend on magnetic field orientation, which can be described by an anisotropic g-tensor.