Optical spin initialization of spin-$\frac{3}{2}$ silicon vacancy centers in 6H-SiC at room temperature

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Silicon vacancies in silicon carbide have been proposed as an alternative to nitrogen vacancy centers in diamonds for spintronics and quantum technologies. An important precondition for these applications is the initialization of the qubits into a specific quantum state. In this work, we study the optical alignment of the spin 3/2 negatively charged silicon vacancy in 6H-SiC. Using time-resolved optically detected magnetic resonance technique, we coherently control the silicon vacancy spin ensemble and measure Rabi frequencies and spin-lattice relaxation time of all three transitions. Then to study the optical initialization process of the silicon vacancy spin ensemble, the vacancy spin ensemble is prepared in different ground states and optically excited. We describe a simple rate equation model that can explain the observed behaviour and determine the relevant rate constants.

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I. INTRODUCTION

Silicon carbide (SiC) exists in nature in many polytypes and hosts many interesting vacancy centers, which have been shown to be useful for applications in quantum technologies like sensing [1,7]. These vacancy centers can be grouped into two classes, depending on their spin in the ground state: $S = 1$ or $S = 3/2$ [3,9]. Neutral divacancies, consisting of neighboring C and Si vacancies, have spin 1. Four different types of divacancies in 4H-SiC have been studied using optical and microwave techniques [7] similar to those used with nitrogen-vacancy qubits in diamond [10,12]. They can be efficiently polarized by optical irradiation and their polarization can be transferred to $^{29}$Si nuclear spins, which are strongly coupled to divacancies in 4H- and 6H-SiC [13]. Coherent control of divacancy spins in 4H-SiC can be achieved even at high temperature up to 600 K [14]. The spins of neutral divacancies in SiC can sensitively detect both strain and electric fields [15], with higher sensitivity than NV centers in diamond [11,15].

Another type of vacancies consists of missing silicon atoms, i.e., silicon vacancies. If they capture an additional electron, they become negatively charged silicon vacancies ($V^-_Si$) and have spin 3/2 [4,8,9,16,17]. Several individually addressable silicon-vacancies have been identified in different SiC polytypes. For example, the 6H-SiC hosts one hexagonal site $h$ and two cubic sites ($k_1$ and $k_2$). $V^-_Si$ at $k_1$ and $k_2$ are called $V_1$ and $V_3$, respectively, whereas $V^-_Si$ at the hexagonal sites $h$ are called $V_2$. The zero phonon lines (ZPL) of these negatively charged vacancies appear at 865 nm ($V_1$), 887 nm ($V_2$), and 908 nm ($V_3$) [17,19]. Optically induced alignment of the ground-state spin sublevels of the $V^-_Si$ in 4H- and 6H-SiC has been demonstrated at room temperature [10]. Coherent control of a single silicon-vacancy spin and long spin coherence times have been reported [2]. $V^-_Si$ are relatively immune to electron-phonon interactions and do not exhibit fast spin dephasing (spin coherence time $T_2 = 0.85$ ms) [20]. Using a moderate magnetic field in combination with dynamic decoupling, the spin coherence of the $V^-_Si$ spin ensemble in 4H-SiC with natural isotopic abundance can be preserved over an unexpectedly long time of >20 ms [21]. Quantum microwave emitters based on $V^-_Si$ in SiC at room temperature [22] can be enhanced via fabrication of Schottky barrier diodes and can be modulated by almost 50% by an external bias voltage [23]. Using all four levels, $V^-_Si$ can be used for absolute dc magnetometry [24].

In our previous work, we studied the temperature-dependent photoluminescence, optically detected magnetic resonance (ODMR), and the relaxation times of the longitudinal and transverse components of the $V^-_Si$ spin ensemble in 6H-SiC, during free precession as well as under the influence of different refocusing schemes [19]. In this work, we focus on the optical spin initialization of the $V_1/V_2$ in 6H-SiC, the spin relaxation and the dynamics of the intersystem-crossing. Section [11] gives details of the sample preparation, and the optical pumping process. Section [12] describes the experimental setup for continuous-wave (cw)- double-resonance and pulsed ODMR measurements. Section [13] describes the measurements of the spin-lattice relaxation rates. Section [14] describes the dynamics of the optical spin alignment. Section [15] contains a brief discussion and concluding remarks.

II. SYSTEM

The experiments were performed on a sample that was isotopically enriched in $^{28}$Si and $^{13}$C. The Si enrichment was performed using gas-centrifuge technology, resulting in an isotopic purity of 99.999%, which was available in the form of small $^{28}$Si pieces (1-3 mm). The $^{13}$C source was carbon powder enriched to 15% in $^{13}$C. The SiC crystal was grown at a temperature of 2300°-2400°C on a
(0001) Si face in an Argon atmosphere at a growth rate of \( \approx 100 \mu \text{m/h} \). After growing the SiC crystal, machining and cutting of the wafer was carried out. The isotope composition was measured by Secondary Ion Mass Spectroscopy (SIMS). The concentrations of \(^{28}\text{Si} \), \(^{29}\text{Si} \), and \(^{30}\text{Si} \) are 99.918 \%, 0.076\%, and 0.006 \%, respectively. The concentrations of \(^{12}\text{C} \) and \(^{13}\text{C} \) are 95.278 \% and 4.722 \%, respectively. To create \( \text{V}_{\text{Si}}^- \) centers, the crystal was irradiated with electrons with a dose of 10\(^{15}\) cm\(^{-2}\) and an energy of 2 MeV at room temperature. In our previous work \([19]\), PL spectra recorded at 5.4 K showed zero phonon lines (ZPL) of the negatively charged vacancies at 865 nm (\( V_1 \)), 887 nm (\( V_2 \)) and 908 nm (\( V_3 \)).

![Energy-level diagram of the 6H-SiC V\(_1\)/V\(_3\) type V\(_{\text{Si}}^-\) showing the ground, excited and shelving states. Radiative transitions are marked by red arrows. The non-resonant laser excitation is shown with an orange arrow. Spin-dependent non-radiative transitions generating the ground-state spin populations are shown as black arrows. The states \( |\pm \frac{3}{2}\rangle_g \) represent ground states, \( |\pm \frac{1}{2}\rangle_e \) the excited states and \( |S\rangle \) the shelving states.](image)

The negatively charged \( V_1 \)/\( V_3 \) type defect in 6H-SiC has spin \( S = 3/2 \) \([8, 9]\). Fig. 1 shows the relevant energy-level diagram in an external magnetic field. The states \( |\pm \frac{3}{2}\rangle_g \) are the spin states of electronic ground state \([17, 22]\) and \( |\pm \frac{1}{2}\rangle_e \) the electronically excited states \([25, 26]\). The shelving state \( |S\rangle \) is an \( S = 1/2 \) state, which is important for the optical pumping process \([25]\) during which it gets populated by intersystem crossing (ISC).

The spin Hamiltonian of the \( S = 3/2 \) states is

\[
\mathcal{H} = D(S_z^2 - \frac{5}{4} I) + g \mu_B \vec{B} \cdot \vec{S},
\]

where the zero field splitting in the electronic ground state is \( 2D = -28 \text{ MHz for } V_1/V_3 \) \([17, 19]\), \( g = 2.0 \) is the electron \( g \)-factor, \( \mu_B \) is the Bohr magneton, \( \vec{I} \) the unit operator, \( \vec{B} \) the external magnetic field, and \( \vec{S} \) is the vector of the electron spin operators. We use a coordinate system whose \( z \)-axis is oriented along the \( C_3 \) symmetry axis, which is the \( c \)-axis of the crystal.

In the absence of optical pumping, when the spin system is in thermal equilibrium at room temperature, all four ground states are almost equally populated. When the system is irradiated with a laser, the populations are re-distributed, and the populations of the spin states \( |\pm \frac{1}{2}\rangle_g \) become large compared to those of \( |\pm \frac{3}{2}\rangle_g \), as shown schematically in Fig. 1 \([22, 25]\). The pumping process starts with the laser driving the transitions from the ground states to the excited states. From there, most of the population falls back to the ground states by spontaneous emission during the excited state lifetime, which is \( \sim 10 \text{ ns in the 6H polytype, estimated form the linewidth of the excited state level anti-crossing (LAC) [27] and } \sim 6.3 \text{ ns in 4H [28]} \). However, the system can also undergo intersystem-crossing (ISC) to the shelving states \( |S\rangle \) \([25]\). The measured time constant from the excited state to \( |S\rangle \) is \( \sim 7.4 \text{ ns for } V_{\text{Si}}^- \) in 4H \([26]\). From there the system returns to the ground state, with a bias for the states \( |\pm \frac{1}{2}\rangle \) over \( |\pm \frac{3}{2}\rangle \), with a time constant 150 ns for \( V_{\text{Si}}^- \) in 4H \([8, 17, 23, 26]\). The exact rates from the excited state to \( |S\rangle \) and from \( |S\rangle \) to the ground state have not been measured yet for \( V_{\text{Si}}^- \) in the 6H-SiC polytype, but they should be close to those in the 4H-SiC polytype. If the spins are not in thermal equilibrium and pumping stops, they relax back to the thermal equilibrium state by spin-lattice relaxation, as shown in Fig. 1. Here, \( \gamma \) and \( \alpha \) are the spin-lattice relaxation rates of the \( |\pm \frac{1}{2}\rangle \leftrightarrow |\pm \frac{3}{2}\rangle \) and \( |\pm \frac{1}{2}\rangle \leftrightarrow |\pm \frac{1}{2}\rangle \) transitions.

**III. OPTICALLY DETECTED MAGNETIC RESONANCE**

The ODMR technique is similar to the conventional electron spin resonance (ESR) technique except for the additional optical pumping and the detection part. In the ODMR technique, instead of measuring absorbed microwave or radio frequency (RF) power, an optical signal is detected, which may by photoluminescence (PL) or a transmitted or reflected laser beam \([12, 29–31]\). Figure 2 shows the setup used for the cw- and time-resolved ODMR measurements. Our light source was a 785 nm laser diode with a maximum power of 400 mW, which was driven by a Thorlabs laser diode controller (LDC202C series) with a thermoelectric temperature controller (TED 200C). For generating the laser pulses, we used an acousto-optical modulator (AOM; NEC model OD8813A). The center frequency of the AOM was 100 MHz, and the RF power was 1.2 W. The RF control signal was generated by a programmable 1 GHz synthesizer HM8133-2 and the RF pulses were
A. Continuous-wave ODMR

To measure the cw-ODMR signal, we used the setup shown in Fig. 2 with the RF switch on for continuous laser irradiation and the APD connected to the lock-in amplifier. The DWG was used to modulate the amplitude of the RF field and the APD signal was demodulated with the lock-in amplifier whose reference signal was supplied by the DWG. Figure 3(b) shows the ODMR signal measured in the absence of a magnetic field by sweeping the DDS-I frequency as the black curve. Two peaks with different signs are observed: a positive one (i.e. increase of the PL at the application of RF) at 28 MHz and a negative one at 128 MHz. The peak at 128 MHz corresponds to the $V_{Si}^−$ at lattice sites $k_2$ ($V_2$ type) and the peak at 28 MHz to $V_{Si}^−$ at the quasi-cubic sites $k_1$ and $k_2$ ($V_1$ and $V_3$ type) which have the same $D$ value. Figure 3(a) shows the energy levels of $V_1/V_3$ as a function of the magnetic field $B$ applied $\parallel c$-axis, calculated from the Hamiltonian given in Eq. (1). Arrows labeled with $\nu_1$, $\nu_2$ and $\nu_3$ represent the transition $|+3/2\rangle \leftrightarrow |+1/2\rangle$, $|1/2\rangle \leftrightarrow |−1/2\rangle$ and $|−3/2\rangle \leftrightarrow |−1/2\rangle$, respectively. With classical ODMR experiments, only one of the three allowed transitions in the spin-3/2 system are observable, since the $±1/2$ states have equal populations. The ODMR signal recorded in a 3.7 mT magnetic field $\parallel c$-axis by sweeping the DDS-I frequency is plotted as the

![Figure 2: Experimental setup for measuring ODMR. The red line from the laser represents the laser beam. The acousto-optical modulator (AOM) generates the laser pulses. Ellipsoids labeled M, L and F represent mirrors, convex lenses, and a long-pass filter, respectively. The RF is applied using three-turn Helmholtz coil-pair made of 100 $\mu$m diameter copper wire placed perpendicular to the c-axis, in series with a 50 $\Omega$ resistor which is represented by a rectangle labeled R. The gray rectangle labeled S is the SiC sample which is placed between the RF coils. The three orthogonal ring-pairs Cx, Cy and Cz represent Helmholtz coils for generating a static magnetic field in arbitrary direction. Rounded rectangles labeled M, L and F represent mirrors, convex lenses, and a long-pass filter, respectively. The RF is applied using three-turn Helmholtz coil-pair made of 100 $\mu$m diameter copper wire placed perpendicular to the c-axis.](image1)

![Figure 3: (a) Energy levels of the $V_1/V_3$ vacancy in a magnetic field $B \parallel c$-axis. (b) ODMR signals vs. frequency. The black curve is the ODMR signal measured in the absence of a magnetic field, the red curve is the ODMR signal in the 3.7 mT magnetic field, and the orange curve is the ODMR with additional 77 MHz RF in the 3.7 mT magnetic field.](image2)
B. Pulsed ODMR

For the time-resolved ODMR, the APD shown in Fig. 2 was connected to the Picoscope USB card. The RF pulses were generated using DDSes and RF switches and applied between the state initialization and measurement.

For all experiments, a laser pulse of 100 mW power and 300 µs duration was used to initialize the V_{Si}, i.e., populating the states |±1/2⟩ more than the states |±3/2⟩. After the polarization of the spin system, a sequence of RF pulses was applied to the system, as discussed in detail below. To read out the final state of the spin system, we applied a second laser pulse of duration 4 µs and integrated the PL collected during the pulse. We averaged the signal 400 times and subtracted it from a 400 times averaged signal of a reference experiment to remove unwanted background signals. This process was repeated 20 times and again the average was taken.

In the following, we assume that the population $\rho_{kk}$ of the ±3/2 spin levels contributes a fraction $\Delta$ more to the PL signal than the ±1/2 spin levels [20,32]. The total PL signal $S$, measured with the second laser pulse, is then

$$S = S_{+3/2} + S_{+1/2} + S_{-1/2} - S_{-3/2}$$

with the contributions

$$S_{+3/2} = (S_0 + \Delta)\rho_{11}$$
$$S_{+1/2} = (S_0 - \Delta)\rho_{22}$$
$$S_{-1/2} = (S_0 - \Delta)\rho_{33}$$
$$S_{-3/2} = (S_0 + \Delta)\rho_{44}$$

from the populations of the different levels, where $S_0$ is the average signal contribution from each level. Taking into account that the sum of the populations is equal 1, this can be further simplified to

$$S = 4S_0 + \Delta(\rho_{11} - \rho_{22} - \rho_{33} + \rho_{44}).$$

(2)

To calibrate the strength of the RF field for the pulsed excitation, we performed a measurement of Rabi oscillations for the $\nu_1$ and $\nu_3$ transitions of the $V_1/V_3$ type $V_{Si}$ using the pulse sequence shown in Fig. 3(a). After the initializing laser pulse, an RF pulse of variable duration $\tau_R$ was applied. The reference signal was obtained from an experiment without an RF pulse.

Rabi oscillations for the $\nu_2$ transition were measured using the pulse sequence shown in Fig. 3(b). Two π pulses with frequency $\nu_1$ were applied, and between them an RF pulse with frequency $\nu_2$ and variable duration $\tau_R$. The reference signal was obtained from an experiment without the RF pulse at $\nu_2$. Figure 3(c) shows the resulting experimental data for the transitions at $\nu_1$, $\nu_2$ and $\nu_3$. The experimental data were fitted to the function

$$S_{RF}(\tau_R) - S_0(\tau_R) = A + B \cos(2\pi\nu_R\tau_R - \phi)e^{-\tau_R/T'_2},$$

(3)

where $S_{RF}(\tau_R)$ is the signal measured with an RF pulse of duration $\tau_R$ and $S_0(\tau_R)$ the reference signal without the RF pulse. The RF power used, Rabi frequencies, and $T'_2$ obtained after fitting are given in Table I.

TABLE I: Parameters of Rabi oscillations for the different transitions of $V_1/V_3$ type $V_{Si}$.

| Transition frequency, RF Power (W) | $\nu_R$ (MHz) | $T'_2$ (ns) |
|----------------------------------|--------------|------------|
| $\nu_1$ (77 MHz)                | 30           | 7.68       |
| $\nu_2$ (101 MHz)               | 36           | 9.81       |
| $\nu_3$ (129 MHz)               | 36           | 8.31       |

FIG. 4: Pulse sequence for measuring Rabi oscillations of (a) $\nu_1$ and $\nu_3$ transitions; (b) $\nu_2$ transition. The red and blue rectangles represent the laser and RF pulses. (c) Experimental Rabi oscillations. The y-axis represents the normalized change of the PL signal and the x-axis the RF pulse duration $\tau_R$. 

red curve in Fig. 3(b). A peak at 77 MHz corresponds to the $\nu_1$ transition, and a peak at 129 MHz corresponds to the $\nu_3$ transition. Due to the equal populations in the $|\pm1/2⟩$ states, the peak for the $\nu_2$ transition is not visible. To observe the transition between them, we added a second RF source to the setup, using it to selectively change the populations. For these experiments, one of the sources was operated at a fixed frequency while the second device was scanned. The output signals of both sources were combined with an RF combiner, amplified and sent to the RF coils. The pump RF field was applied at frequency $\nu_1$ and the inset of Fig. 3(b) shows the modified populations. Sweeping the second DDS, we recorded the ODMR signal plotted as the orange curve in Fig. 3(b) where the $\nu_2$ transition appears at 101 MHz.
IV. POPULATION RELAXATION

A. Equation of motion

The uncontrolled interaction of a spin system with its environment has two effects on a system that has been excited from its thermal equilibrium state: it causes dephasing, i.e., loss of coherence, and a return of the system to the thermal equilibrium state [33], which is known as spin-lattice relaxation. In this process, energy is exchanged between the system and its environment (the lattice). As shown in Fig. 1 due to energy exchange between the $V_{Si}$ and their environment, the populations evolve towards the equilibrium distribution with rates $\alpha$ and $\gamma$, where $\alpha$ is the rate at which the $|\pm \frac{3}{2}\rangle$ spin levels equilibrate, and $\gamma$ is the rate between the $|\pm \frac{3}{2}\rangle g \leftrightarrow |\pm \frac{1}{2}\rangle g$ states. The time evolution of the four level system can thus be described by the following equation:

$$ \frac{d}{dt} \vec{\rho} = \frac{1}{2} \begin{pmatrix} -\gamma & -\alpha & -
\end{pmatrix} \vec{\rho}, \quad (4) $$

where the population vector $\vec{\rho}$ contains the diagonal elements $\rho_{ii}$ of the density operator. The eigenvalues $\lambda_i$ and eigenvectors $\vec{u}_i$ for Eq. (4) are

$$ \vec{\lambda} = \begin{pmatrix} 0 & \frac{\gamma}{\alpha + \gamma} & \frac{\xi}{2} \\
\frac{\alpha + \gamma}{\alpha + \gamma} & \frac{\alpha + \gamma}{\alpha + \gamma} & \frac{\xi}{2} \\
\frac{\alpha + \gamma}{\alpha + \gamma} & \frac{\alpha + \gamma}{\alpha + \gamma} & \frac{\xi}{2} \end{pmatrix} $$

and

$$ \vec{u}_i = \begin{pmatrix} 1 \\
1 \\
1 \end{pmatrix}, \begin{pmatrix} 1 \\
-1 \\
1 \end{pmatrix}, \begin{pmatrix} -\gamma \\
\alpha + \xi \\
\gamma \end{pmatrix}, \begin{pmatrix} -\gamma \\
-\alpha - \xi \\
\gamma \end{pmatrix} $$

respectively, where $\xi = \sqrt{\alpha^2 + \gamma^2}$.

The solution of Eq. (4) for an initial condition $\vec{\rho}(0) = (a, b, c, d)^T$ is

$$ \vec{\rho}(t) = \frac{1}{4} \sum c_i e^{\lambda_i t} \vec{u}_i \quad (5) $$

where the weights

$$ c_1 = 1 $$
$$ c_2 = a - b - c + d $$
$$ c_3 = \frac{(a - d)(\alpha - \xi) + \gamma(b - c)}{\gamma \xi} $$
$$ c_4 = -\frac{(a - d)(\alpha + \xi) + \gamma(b - c)}{\gamma \xi} $$

are given by the initial conditions.

B. Measurements

High-quality measurements of the time dependence of individual populations are difficult. We therefore measure differences $\rho_{ii} - \rho_{kk}$ between populations. We start with two particularly simple time-dependences, which can be measured with the experiment shown in Fig. 5 (a) and (b). We first prepare an initial state with the populations $\vec{\rho}_i(0) = (0, 0.5, 0.5, 0)^T$, so that $c_1 = c_2 = 1$ and the expected time-dependence is

$$ \vec{\rho}(t) = \frac{1}{4} (\vec{u}_1 - e^{\lambda_1 t}\vec{u}_2) = \frac{1}{4} \begin{pmatrix} 1 - e^{-\gamma t} \\
1 + e^{-\gamma t} \\
1 + e^{-\gamma t} \\
1 - e^{-\gamma t} \end{pmatrix} \quad (6) $$

The pulse sequence for the preparation of the initial state $\vec{\rho}_i(0)$ from the unpolarized state is shown in the first row of table 1. It consists of a laser pulse of duration 300 $\mu$s. After the state preparation, the system is allowed to relax for a time $\tau_1$. To read out the final state, we apply an RF pulse with flip-angle $\pi$ and record the PL during the measuring laser pulse. We subtract the result of this
experiment from a similar experiment where the RF pulse was omitted. The resulting signal is proportional to the difference between the populations that were exchanged by the π pulse. If the π-pulse is applied at frequency \( \nu_1 \), the signal is proportional to \( \rho_{22}(\tau_1) - \rho_{11}(\tau_1) \) and if it is applied at \( \nu_3 \), the signal is proportional to \( \rho_{33}(\tau_1) - \rho_{44}(\tau_1) \).

Figure 6 (c) shows the resulting signals for \( \rho_{22}(\tau_1) - \rho_{11}(\tau_1) \) and \( \rho_{33}(\tau_1) - \rho_{44}(\tau_1) \) as a function of the delay \( \tau_1 \). We fit the theoretical signal of Eq. (6) to the experimental signal. From the fits, we obtain the relaxation rate \( \gamma = 6.8 \pm 0.2 \text{ ms}^{-1} \) and the relaxation times \( T_1^{22} = T_1^{33} = 1/\gamma = 146.2 \pm 3.6 \text{ µs} \).

To determine the second rate constant \( \alpha \), a different initial condition is needed. We chose \( \vec{\rho}_{22}(0) = (0.5, 0.5, 0, 0) \) and measured the population difference \( \rho_{22} - \rho_{33} \), which we expect to depend on the relaxation delay \( \tau_1 \) as

\[
\rho_{22}(\tau_1) - \rho_{33}(\tau_1) = \frac{\lambda_3(\alpha - \xi)e^{\lambda_1\tau_1} - \lambda_3(\alpha + \xi)e^{\lambda_3\tau_1}}{2\gamma\xi}. \tag{7}
\]

The pulse sequence used to prepare the initial state \( \vec{\rho}_2(0) \), from the thermal state is given in row 2 of Table III and in Figure 5 (b) which also shows the sequence for measuring the population difference \( \rho_{22} - \rho_{33} \). For the initial state preparation, the 300 µs laser pulse, and two RF π pulses were applied, with one frequency \( \nu_1 \) and a second with frequency \( \nu_2 \). Then the system was allowed to relax for a time \( \tau_1 \) and another RF π-pulse with frequency \( \nu_1 \) and the measuring laser pulse were applied. The result of this experiment was subtracted from a reference experiment with an additional π pulse of frequency \( \nu_2 \) after the delay \( \tau_1 \), as indicated in Fig. 5 (b) by the dashed rectangle. Fig. 5 (d) shows the resulting signals for \( \rho_{22}(\tau_1) - \rho_{33}(\tau_1) \) as a function of the delay \( \tau_1 \). The theoretical signal of Eq. (7) was fitted to the experimental signals, using the value of \( \gamma \) determined before. From the fits, we obtained the relaxation rate \( \alpha = 9.3 \pm 0.4 \text{ ms}^{-1} \) and the relaxation time \( T_1^{33} = 1/\alpha = 107.3 \pm 4.9 \text{ µs} \).

V. OPTICAL SPIN ALIGNMENT

### A. Experiments

Initialization of quantum registers to a specific state is one of the primary requirements for the realization of any quantum device [34][35]. The \( V_{Si} \) spin ensemble can be initialized into the \( \pm 1/2 \) spin states of the electronic ground-state by laser illumination [19][22][25]. To determine the dynamics of this initialization process, we prepared the spin ensemble in different initial states, applied a laser pulse and again measured the populations \( \vec{\rho}(t) \) as a function of the duration of the laser pulse. Figure 6 shows the pulse sequence used for preparing and measuring the population differences \( \rho_{ii} - \rho_{jj} \) during optical pumping. First, we started with the unpolarized state \( \vec{\rho}_0(0) = (1/4)(1, 1, 1, 1) \)T. The laser pulse of duration \( t \) was applied, followed by the RF sequence given in Table III and the PL signal was measured during the readout pulse. This PL signal was subtracted from a reference PL signal measured by a similar experiment where no RF pulse was applied. The difference signal is proportional to \( \rho_{ii} - \rho_{jj} \). For measuring the population differences \( \rho_{22} - \rho_{11} \) and \( \rho_{33} - \rho_{44} \), the same RF pulse sequences were used as in Sec. IV B. For measuring the population difference \( \rho_{33} - \rho_{44} \), the RF pulse sequence given in the third row of Table III was used i.e., a π pulse with frequency \( \nu_2 \) followed by a π pulse at frequency \( \nu_3 \). For measuring the population difference \( \rho_{33} - \rho_{11} \), the RF pulse sequence is given in the fourth row of Table III. A π pulse at frequency \( \nu_2 \) is followed by another π pulse at frequency \( \nu_3 \). The experimental data \( (S_{\rho_{ii} - \rho_{jj}}(t)) \) were scaled by multiplying them with a constant factor \( N \) such that the signal for \( \rho_{33} - \rho_{44} \) of the stationary state \( |0\rangle \) prepared by a 300 µs laser pulse matches the theoretically expected value of 0.37.

\[
\rho_{ii} - \rho_{jj}(t) = NS_{\rho_{ii} - \rho_{jj}}(t). \tag{8}
\]

While the absolute scale of the signal is not important for the goal of determining the rate constants, we use this scaling which fixes the absolute values of the populations and allows a unique comparison between the theoretical model and the experimental data. The resulting normalized signals \( \rho_{ii} - \rho_{jj} \) are shown in Fig. 7(a).

All four populations \( \rho_{11}, \rho_{22}, \rho_{33} \) and \( \rho_{44} \) could be determined individually from the four experiments described above and using normalization condition i.e.,
ρ_{11} + ρ_{22} + ρ_{33} + ρ_{44} = 1.

Figure 7(b) shows the evolution of the populations of the spin states during the laser pulse. Starting from the unpolarized state where all populations are \(ρ_{ii} = \frac{1}{4}\), the populations \(ρ_{22}\) and \(ρ_{33}\) grow to a limiting value of \(\approx 0.44\) while the populations \(ρ_{11}\) and \(ρ_{44}\) decrease to a limiting value of \(\approx 0.06\).

We repeated the experiment of Fig. 6 with different initial conditions: \(\vec{ρ}_{0}(0) = (0, 0.5, 0.5)^T\) and \(\vec{ρ}_{0}(0) = (0, 0, 0.5, 0.5)^T\). The pulse sequences used for the preparation of these initial states are given in the third and fourth row of Table 7 respectively. The corresponding results are shown in figures 8(a) and (b). From the measured populations differences, we reconstructed the time-dependence of the populations, which are shown in Fig. 8(c) and (d), as a function of the laser pulse duration \(t\). The experimentally prepared initial states were \(\vec{ρ}_{exp}(0) = (0.03, 0.47, 0.11, 0.39)^T\) and \(\vec{ρ}_{exp}(0) = (0.06, 0.16, 0.36, 0.42)^T\). One of the main reasons for the deviations of the experimentally prepared states from the theoretical states is the low laser intensity, which results in incomplete polarisation. This could be improved by using a tighter focus of the laser beam. Other causes are imperfections in the RF pulses and relaxation.

\[\frac{d}{dt} \vec{ρ} = \begin{pmatrix} -γ - 2δ & γ & γ & δ \\ 2δ & -γ + δ & -α + γ & 0 \\ -α - γ - δ & -α - γ - δ & -γ + δ & -γ + 2δ \end{pmatrix} \vec{ρ}\]

where \(δ\) is the rate at which population is pumped from the \(|±\frac{3}{2}\rangle\) through the shelving state to \(|±\frac{1}{2}\rangle\), as indicated in Fig. 8(b). Figures 7 and 8 show that during the laser pulse, the populations of the \(|±\frac{1}{2}\rangle\) states increase to values close to 0.5, while the populations of the \(|±\frac{3}{2}\rangle\) states are almost completely depleted.

Based on these experimental results and assuming that the lifetimes in the excited state and the shelving states are short compared to the pumping time, we use the following equations for modeling the dynamics of the system:

\[\vec{ρ}_{st} = \frac{γ}{4(γ + δ)} \begin{pmatrix} 1 & 0 \\ 1 & 1 \\ 1 & 0 \end{pmatrix} + \frac{δ}{2(γ + δ)} \begin{pmatrix} 0 & 1 \\ 1 & 1 \end{pmatrix},\]

which approaches \((0, \frac{1}{2}, \frac{1}{2}, 0)^T\) for \(δ \gg γ\).

The eigenvalues and eigenvectors for Eq. 9 are

\[\vec{λ}^{op} = \begin{pmatrix} 0 \\ -α - γ - δ \\ -α + γ + δ - δ \\ α + γ - δ - δ \end{pmatrix}\]
where \( \delta = 39 \pm 3 \text{ ms}^{-1} \). For \( \alpha \) and \( \gamma \), we used the values determined in section IV.

The resulting expressions for the case where the initial state is the depolarised state is given in Appendix A. The calculated population differences are plotted in Figures 7 (a), 8 (a), and (b), and the populations in Figures 7 (b), 8 (c) and (d). The best fits with the experimental data, which were measured with a laser intensity \( I \), as shown in Figure 8 (a).

VI. DISCUSSION AND CONCLUSION

Silicon vacancy centers in SiC have shown promising results for quantum sensing, single-photon emitters, and applications as light-matter interfaces and other quantum technologies. In this work, we have demonstrated the coherent control of all four levels of the \( V_{1}/V_{3} \) type \( V^{	ext{SI}} \). We measured the Rabi frequency of all three RF transitions and the relaxation rates, i.e., \( \alpha \) and \( \gamma \) of the transitions \(|\pm 3/2 \rangle \leftrightarrow |\pm 1/2 \rangle \) and \(|\pm 1/2 \rangle \leftrightarrow |\pm 1/2 \rangle \) by fitting the data with the proposed relaxation model. We also determined the dynamics of the optical initialization process by preparing the system in three different initial states and measuring the population dynamics during the laser pulse. We proposed a simple rate equation model for this process and were able to determine all relevant rate constants from the experimental data. We are confident that these results will contribute to a better understanding of this fascinating system and open the way to more useful applications.

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Appendix A: Time dependences for specific initial conditions

This section provides two specific solutions for the population dynamics without and with the laser field, for 2 different initial conditions. For the initial state \( \rho_{2}(0) = \frac{1}{4}(1, 1, 0, 0)^{\top} \), the solution of the relaxation dynamics Eq. (6) is
\[
\begin{align*}
\rho_{11}(t) &= \frac{\lambda_3 e^{\lambda_3 t} + \lambda_4 e^{\lambda_4 t} + \xi}{4\xi}; \\
\rho_{22}(t) &= \frac{\lambda_3 (\alpha - \xi) e^{\lambda_3 t} - \lambda_4 (\alpha + \xi) e^{\lambda_4 t} + \gamma \xi}{4\gamma \xi}; \\
\rho_{33}(t) &= \frac{\lambda_3 (-\alpha + \xi) e^{\lambda_3 t} + \lambda_4 (\alpha + \xi) e^{\lambda_4 t} + \gamma \xi}{4\gamma \xi}; \\
\rho_{44}(t) &= \frac{-\lambda_3 e^{\lambda_3 t} + \lambda_4 e^{\lambda_4 t} + \xi}{4\xi}.
\end{align*}
\]

For the initial state \(\rho_0(0) = \frac{1}{2} (1, 1, 1)^T\), the solution of the optical pumping dynamics Eq. (11) is

\[
\begin{align*}
\rho_{11} &= \rho_{44} = -\frac{\gamma + \delta e^{2\gamma t}}{4\lambda_2^op}, \\
\rho_{22} &= \rho_{33} = -\frac{\gamma - 2\delta - \delta e^{2\gamma t}}{4\lambda_2^op},
\end{align*}
\]

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