Multi-photon multi-quantum transitions in the spin-$\frac{3}{2}$ silicon-vacancy centers of SiC

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Vacancies in silicon carbide (SiC) are excellent candidates for quantum sensing and technology applications [1–5] as they can be controlled coherently and have long spin coherence times [6–8]. Apart from that, mature fabrication techniques exist for SiC. Here we focus on the silicon vacancies in the 6H-SiC polytype [9–11], where three types of Si vacancies have been identified, labelled $V_1$, $V_2$ and $V_3$, which correspond to different lattice positions [5,12,13]. It has been shown that silicon-vacancies at hexagonal sites $h$ correspond to $V_1$, while $V_3$ and $V_2$ are at cubic lattice sites $k_1$ and $k_2$ [14]. When the vacancies are negatively charged ($V_{Si}^-$), they have spin 3/2 and the ground state spin sublevels can be polarized by optical irradiation [10,11]. In previous work, we measured relaxation rates and optical spin initializations of $V_{Si}^-$ at room temperature [9,10], the polarization dependencies of the ZPLs and the ODMR contrast as a function of temperature [15].

$I$. INTRODUCTION

Silicon vacancy centers in silicon carbide are promising candidates for storing and manipulating quantum information. Implementation of fast quantum gates is an essential requirement for quantum information processing. In a low magnetic field, the resonance frequencies of silicon vacancy spins are in the range of a few MHz, the same order of magnitude as the Rabi frequencies of typical control fields. As a consequence, the rotating wave approximation becomes invalid and nonlinear processes like the absorption and emission of multiple photons become relevant. This work focuses on multi-photon transitions of negatively charged silicon vacancies driven by a strong RF field. We present continuous wave optically detected magnetic resonance (ODMR) spectra measured at different RF powers to identify the 1-, 2-, and 3-RF photon transitions of different types of the silicon vacancy in the 6H-SiC polytype. Time-resolved experiments of Rabi oscillations and free induction decays of these multiple RF photon transitions were observed for the first time. Apart from zero-field data, we also present spectra in magnetic fields with different strength and orientation with respect to the system’s symmetry axis.

$V_{Si}^-$ in 6H-SiC have smaller crystal field splittings than nitrogen vacancies in diamond. Even at modest radio frequency (RF) powers, the spin Rabi frequencies are in the MHz range and thus comparable to the resonance frequency in zero or low magnetic field. Hence, the RF field drives not only the allowed single-photon transitions, but we also find absorption of multiple photons, aperiodic evolution of the system and nonlinear dependencies of effective Rabi frequencies on the applied RF strength. A multi-photon transition occurs by simultaneous absorption and emission of multiple photons such that the transition frequency corresponds to an integer multiple of the driving RF frequency. Two-photon transitions have been studied in different systems [16,19] including NMR of spin-1 system [20]. The two RF photon absorption between two spin states differing by $\Delta m_S = 2$ has also been observed in $V_{Si}^-$ [8]. Further, the absorption of a single photon causing a weak transition with $\Delta m_S = 2$ was also observed in the $V_2$ type vacancies of $4H$-SiC [21]. The authors mentioned as a possible cause of these transitions stray magnetic fields not aligned with the c-axis or the hyperfine interaction of the $V_{Si}^-$ with nuclear spins which lead to a mixing spin levels and make the double quantum transitions, which are normally forbidden, weakly allowed. Later, it has been demonstrated that the amplitude of the double-quantum transitions of $V_{Si}^-$ was the same in natural and isotopically purified $4H$-SiC samples [22]. These authors considered additional terms in the spin Hamiltonian due to the trigonal pyramidal symmetry of this center as the cause of these double-quantum spin transitions [22].

Figure 1 shows a typical experimental spectrum of the $V_3$ vacancy in magnetic field of 4.5 mT $\parallel$ c-axis with a number of transitions that do not match the “allowed” magnetic dipole transitions. The resonances marked 1 and 2, which are found at the lowest frequencies, are 3-photon transitions between spin states with $\Delta m_s = 1$ while peaks 5 and 6 are due to the 2-photon transitions between spin levels with $\Delta m_s = 2$. The peak labelled with 7 in Fig. 1 is due to a single-photon, 2-quantum transition between the spin levels 3/2 $\leftrightarrow$ 1/2.

This work explores the possible multi-photon and multiple quantum transitions of the $V_{Si}^-$ in the 6H-SiC using continuous wave and pulsed ODMR techniques. We numerically simulate the stationary and time-dependent system response through a master equation for the $V_{Si}^-$ spin ensemble. The results are in excellent agreement with the experimental observations.

This paper is organized as follows. Section II introduces the properties of the spin system. The first subsection of Sec. III provides some details about continuous wave optically detected magnetic resonance (cw-ODMR) experiments at different RF powers. The second subsection shows time-resolved measurements of 1-, 2-, and 3-RF photon transitions. Section IV provides some details about the simulations. Section V A contains the ODMR recorded in the presence of magnetic fields. Fi-
the field is linearly polarized, other values correspond to elliptical (including circular) polarization.

When the $V_{\text{Si}}$ are irradiated with a suitable wavelength laser, population is transferred to the excited state. Most of the population falls back to the ground state by spontaneous emission, but some of it undergoes intersystem crossing (ISC) to the shelving states and preferentially returns to specific ground-state spin-levels depending upon the type of vacancies $[5, 9, 23]$: in $V_2$ ($V_3$), the population preferably falls into the $\pm 3/2$ ($\pm 1/2$) spin states $[10]$.

Another process that affects the dynamics of the silicon-vacancy is spin relaxation: spin-lattice ($T_1$ relaxation) and spin-spin relaxation ($T_2$ relaxation). We studied these relaxation processes at room temperature and determined the corresponding relaxation rates in previous works $[9, 10]$.

### III. OPTICALLY DETECTED MAGNETIC RESONANCE

Optically detected magnetic resonance (ODMR) is a technique for measuring electron spin resonance (ESR) through an optical signal instead of inductive detection $[24, 25]$. The optical irradiation establishes a non-thermal population of the different spin states. Since the different spin states contribute differently to the photoluminescence (PL) rate, a change in the spin polarization leads to a change of the PL rate, which can be used to measure the spin polarization. The sensitivity of this technique is often high enough to measure ODMR of individual electron spins $[3, 25, 27]$. We used the same technique for measuring the ODMR of silicon vacancies in 6H-SiC with natural isotopic composition. Additional details of the ODMR setup are given in Appendix B.

#### A. Continuous-wave ODMR

In our continuous-wave (CW) ODMR experiments, the sample was continuously illuminated with 785 nm laser light while the RF field was modulated (switched ON /
OFF). The PL from the sample was collected and detected by an avalanche photodiode (APD) module after passing through a 850 nm long-pass filter. The electrical signal from the APD was recorded by a lock-in amplifier referenced to the ON/OFF modulation signal [3][10]. Figures 1 and 2(a) show two such spectra, which were recorded at room temperature, in a field of 4.5 mT (Figure 1) and 0 (Figure 2(a)), respectively, by recording the lock-in signal as a function of the RF frequency. At low RF power, two peaks are visible in the zero-field spectrum of Figure 2(a), a positive one at 28 MHz (P₁) and a negative one at 128 MHz (P₂), which correspond to the V₃ and V₂ sites of V₂. A positive signal corresponds to an increase in the PL when the RF field is resonant. As the RF power is increased, the amplitude and width of these peaks increases and additional peaks become visible at 9 MHz (P₂), 14 MHz (P₂), 43 MHz (P₃), and 64 MHz (P₄). The resonance lines marked P₁ (P₃) and P₂ (P₄) appear at one-third and one-half to the frequency of the V₃ (V₂) peaks. The peak P₃ at 43 MHz overlaps with P₁.

The different peaks show remarkably different power dependence as shown in Figure 2(b), which represents the ODMR signal amplitude vs. the square root of the applied RF power of all peaks except P₂ (which is difficult to extract, due to the overlap). The experimental data were fitted with the function

\[ S(\Lambda) = S_{\text{max}} (\Lambda^c/\Lambda_0 + \Lambda^c), \]

where \( S(\Lambda) \) is the ODMR signal amplitude and \( \Lambda \) the square root of RF power. The exponent \( c \) is set to 1, 2 and 3 for the 1-, 2- and 3-photon transitions. If the exponent \( c \) is used as an additional fitting parameter, the optimal fit is obtained with values that are close to these. The values for \( S_{\text{max}} \) and \( \Lambda_0 \) for the different peaks are given in Table I.

**B. Time-resolved experiments**

For measuring Rabi oscillations and free induction decays with 1-, 2-, and 3 RF photon excitation, we used time-resolved ODMR. A typical time-resolved ODMR experiment consists of an initial laser pulse, which polarizes the spin ensemble. Then, a set of RF pulses and delays are applied before measuring the PL with a measuring laser pulse. We will start with the Rabi oscillation.

**FIG. 3.** (a) Pulse sequence for measuring Rabi oscillations. (b) Rabi oscillations measured for V₃ with 1-, 2- and 3 RF photons at room temperature. Circles, diamonds and squares represent experimentally measured data. Red curves are the simulations obtained by solving Eq. 7 numerically for different photons transitions. The curves have been shifted vertically to avoid overlap.

1. Rabi oscillations

Figure 3 (a) shows the pulse sequence for measuring Rabi oscillations for the different transitions. The spin ensemble was first polarized with a 300 µs laser pulse. A signal was recorded during a 4 µs laser pulse after an RF pulse of variable duration \( \tau_R \). The same experiment was repeated without the RF pulse to obtain a reference signal to suppress background signals. The signals obtained from both experiments were subtracted from each other for each pulse duration \( \tau_R \) [9][10]. Figure 3 (b) shows the Rabi oscillation recorded in zero magnetic field for the V₃ type with 1-, 2- and 3-RF photon transitions at room temperature. For measuring Rabi oscillations of the 1 photon transition, a 28 MHz linearly polarized RF pulse of 11 W was applied, whereas 14 MHz (9.3 MHz) was used for the 2 (3) photon transition with the same RF power. The red curves in Fig. 3 (b) are signals calculated for the 1 photon (\( \omega=28 \) MHz), 2 photon (\( \omega=14 \) MHz), and 3 photon (\( \omega=9.3 \) MHz) transitions. More details about the simulations of the curves are given in subsection IV A.

2. Free Induction decay

Figure 4 (a) shows the pulse sequence for measuring free induction decays (FIDs). As above, we initialized the spin ensemble by a first laser pulse and a first RF pulse with a frequency of 28 MHz, 14 MHz, and 9.3 MHz for 1-, 2-, and 3 photon transitions and duration 25 ns for all cases. During the subsequent delay \( \tau_f \), the coherence generated by the pulse was allowed to precess freely. A second RF pulse with the same frequency and duration, and phase \( \phi_d = 2\pi f_{\text{det}} \tau_f \) (detuning frequency \( f_{\text{det}}=40 \) MHz) was applied before the readout laser pulse. We again used the difference between two experiments, where the second RF pulses have phases \( \phi_d \) and \( \phi_d + \pi \), respectively, to suppress unwanted background signals [9][10].

**TABLE I.** Fitting parameters of Eq. 3 for the different ODMR peaks P₂ for the V₂ and V₃ vacancies.
Laser
RF
300 µs 4 µs
τf
±x + φdx
RF

Figure 4 (b) shows the experimentally recorded FIDs with the 1-, 2-, and 3 RF photon pulses in zero magnetic field and at room temperature. The recorded experimental data were fitted with the function:

\[
S_{x+\phi_{d}}^{N} - S_{x+\phi_{d}}^{N} = A \cos(2\pi f - \phi) e^{-\tau f / T_{2}^*},
\]  

where \(S_{x+\phi_{d}}^{N}\) and \(S_{x+\phi_{d}}^{N}\) are signals recorded with \(N\)-photon pulses in the main and reference experiment. The values obtained for the frequency \(f\) are 40.0±0.1 MHz, 53.3±0.2 MHz, and 56.1±0.5 MHz for 1-, 2-, and 3 photon FID measurements respectively; and the average dephasing rate \(T_{2}^*\) is 62.0±5.6 ns. In these experiments, the signal frequency \(f\) is the difference between the transition frequency (2\(D\) = 28 MHz) and the sum of the RF frequency \(f_{RF}\) and the detuning frequency \(f_{det}\) : \(f = |2D - (f_{RF} + f_{det})|\).

IV. SPIN DYNAMICS

The dynamics of the closed spin system can be estimated using the Liouville–von Neumann equation:

\[
\frac{\partial \rho}{\partial t} = -2\pi i [\mathcal{H}(t), \rho],
\]  

where we use units with \(\hbar = 1\), \(\rho\) is the spin density matrix, \(\mathcal{H}(t) = \mathcal{H} + \mathcal{H}_{RF}(t)\) is the total Hamiltonian, i.e., the sum of the static system Hamiltonian \(\mathcal{H}\) given in Eq. (1) and the time-dependent RF Hamiltonian \(\mathcal{H}_{RF}(t)\) in the laboratory frame which is given in Eq. (2). We solve it numerically using the Runge-Kutta 4 method, without invoking the rotating wave approximation to include higher-order contributions.

A. Coherent Evolution

Figure 5 shows the simulation results obtained using equation Eq (5) (ignoring relaxation processes), with a diagonal initial state \(\rho_{0} = \{0, 0.5, 0.5, 0\}\), RF coupling strength \(\Omega_{1} = 9.1\) MHz, using the RF Hamiltonian given in Eq (2) with \(\phi = 0\) for linear and \(\phi = \pi/4\) for left circular \((\sigma^{-})\) polarized RF. Figure 5 (a) and (b) shows the population dynamics of \(V_{5}\) with the absorption of 2 \((\omega = 14\) MHz) and 3 \((\omega = 9.3\) MHz) linearly polarized RF photons, respectively. In comparison, Figure 5 (c) and (d) shows the population dynamics for the system interacting with a left circularly \((\sigma^-)\) polarized RF field resonant with the 2- and 3-photon transitions. The circularly polarised field breaks the symmetry observed in Fig. 5 (a) and (b) by exciting mostly the spin transition 1/2\(\leftrightarrow\)3/2 with \(\Delta m_{S} = 2\) in the case of 2-photon absorption and the transitions 1/2\(\leftrightarrow\)3/2 and -1/2\(\leftrightarrow\)3/2 with \(\Delta m_{S} = 2\) and \(\Delta m_{S} = 1\) in the case of 3-photon excitation. This is in contrast to the linearly polarized field which couples equally to 1/2\(\leftrightarrow\)3/2 and -1/2\(\leftrightarrow\)3/2 and to 1/2\(\leftrightarrow\)3/2 and -1/2\(\leftrightarrow\)3/2.

Since the strength of the RF field is comparable to the transition frequency, the relation between field strength and the observed dynamics is highly nonlinear. As shown in Figure 5, the oscillations of the populations contain multiple frequencies. Fourier-transformation shows that they consist of a small number of frequencies whose amplitudes and positions shift with increasing RF field strength. As a comparison with typical resonant excitations (Rabi-flopping), we perform Fourier transforms of the time-traces and consider the main frequency compo-
environment interaction has two main effects on the system, which is not in its thermal equilibrium state. The first is the loss of coherence, also called spin-spin relaxation, which preserves the energy of the system. It can be taken into account by a term $\dot{\rho}_{ik} = -\frac{\rho_{ik}}{T_{2ik}}$ in the equation of motion. The second effect is that the populations relax back to thermal equilibrium by a process called spin-lattice relaxation. In this process, energy is exchanged between the system and its environment (the lattice) [28]. This contribution can be taken into account as $\dot{\rho} = M\rho$, where the population vector $\rho$ includes the diagonal density operator elements and the transition matrix $M$ depends on the mechanism that couples the system to the environment. Here, we assume that the spin levels 1/2 and -1/2 equilibrate with a rate $\alpha$ and spin levels $\pm 3/2$ and $\pm 1/2$ equilibrate with a rate $\gamma$. This corresponds to the transition matrix

$$M = \begin{pmatrix}
-\gamma & \gamma \\
-\alpha - \gamma & \alpha \\
-\alpha - \gamma & \gamma
\end{pmatrix}.$$  

In our previous work [9], we determined these spin relaxation rates for the $V_1$ type of $V_{\text{Si}}$ and found that the ratio $\alpha/\gamma$ agrees with the theoretical value of 4/3. We also studied the dynamics of the optical initialization process and found that the laser illumination transfers the population from $\pm 3/2$ to $\pm 1/2$ with a pumping rate $\delta$, which is proportional to the laser intensity [9]. Figure 7 shows the optical pumping and relaxation schemes used for the silicon vacancies. The ground, excited, and shelving states are labeled $|g\rangle$, $|e\rangle$, and $|s\rangle$. The nonresonant laser excitation is shown with a thick red arrow. When the vacancy is excited with the laser light, most of the population falls back from the electronically excited state to the ground state by spontaneously emitting photons. The system can also undergo ISC to the shelving states, from where it preferentially to the spin levels $\pm 1/2$ ( $\pm 3/2$ ) of the electronic ground state in case $V_3$ ($V_2$). An optical pumping rate $\delta$ is the rate at which population is pumped from the electronic ground state spin levels $\pm 3/2$ to $\pm 1/2$ in case of $V_3$ and vice versa for $V_2$ [9][10].

For the numerical simulation, we use the Lindblad master equation

$$\frac{\partial \rho}{\partial t} = -2\pi i [H_\text{p}(t), \rho] + \sum_{\alpha,\beta,i,j} L_\alpha^i \rho L_i - \frac{1}{2} \left( L_\alpha^i L_i \rho + \rho L_i \right)$$

where $L_\alpha = \sqrt{2} \begin{pmatrix}
0 & \sqrt{\gamma} \\
0 & \sqrt{\alpha} \\
0 & \sqrt{\gamma}
\end{pmatrix}$ (taking into account $\gamma = 3\alpha/4$) drives the spin-lattice relaxation process. $L_\beta = \sqrt{2\beta} S_z$ is the Lindblad operator for the dephasing process, and $L_{\delta i,j}^\alpha$ are the Lindblad operators for the optical pumping. The matrix forms of the other Lindblad operators are given in APPENDIX C.

The red curves in Fig. 4 (b) of subsection III B 1 are signals calculated as $0.5(1+\rho_{11}^2+\rho_{22}^2+\rho_{33}^2+\rho_{44}^2)$ from Eq 7.
for 1 photon- (ω=28 MHz), 2 photon- (ω=14 MHz), and 3 photon- (ω=9.3 MHz) transitions, with an initial diagonal state \( \rho_0 = \{0, 0.5, 0.5, 0\} \). RF coupling strength \( \Omega_1 = 9.1 \) MHz, using the RF Hamiltonian given in Eq. (2) with \( \phi = 0 \) for a linearly polarized RF field and using the Runge-Kutta 4 method. Additional details are given in Appendix C. To simulate the effect of RF inhomogeneity, signals with 0.97, 1 and 1.03 times \( \Omega_1 \) were calculated and added with weights 0.3, 0.4 and 0.3, respectively. The values of the relaxation rate was \( \alpha \) and added with \( \beta = 0 \) for a linearly polarized RF field. The rates \( \phi \) for time \( t = 4 \) ns in 8000 time steps, using the RF Hamiltonian \( \mathcal{H}_R(t) = \mathcal{H} + \mathcal{H}_RF(t) \) for 4 µs and plotted the resulting signal as a function of the RF frequency. The ODMR signal was calculated as the difference \( S_{RF} - S_0 \) between the signal \( S_{RF} \) with applied RF field and the reference signal \( S_0 \). Each part was calculated from the diagonal elements of the stationary density matrix as \( S_{RF} = \rho_{11} - \rho_{22} - \rho_{33} + \rho_{44} \) [29], where \( \rho_{11}, \rho_{44} \) and \( \rho_{22}, \rho_{33} \) are the populations of the spin levels \( |\pm 3/2\rangle \) and \( |\pm 1/2\rangle \), respectively.

Figure 9 (a) shows the simulated ODMR signal at different RF coupling strengths \( \Omega_1 \) vs RF frequency \( \omega \) obtained by numerically solving Eq. (7) with a diagonal initial state \( \rho_0 = \{0, 0.5, 0.5, 0\} \) \( (\gamma_1, \gamma_2, \gamma_3) = (\gamma_1, \gamma_2, \gamma_3, \gamma_2, 0) \) for \( V_2 \). The rates \( \gamma_1, \gamma_2, \gamma_3 \) were extracted from experimental data: the spin-lattice relaxation rate \( \gamma_1 = 10.8 \) ms\(^{-1} \) (9.3 ms\(^{-1} \)) for \( V_2(V_3) \), as determined in our earlier works [9, 10]. Under the influence of an RF field, the dephasing is slower than during free precession and depends on the homogeneity of the RF field. We therefore estimated it from the Rabi measurements at different RF powers. For low power, the dephasing rate decreases linearly with increasing RF power and then increases linearly in both types of vacancies. This indicates that the RF field decouples the vacancy spin from nuclear spins coupled by hyperfine interactions, while at higher power, the effect of RF inhomogeneity starts to dominate. Further, the dephasing rate also depends on the applied static magnetic field to the \( V_2 \) [21]. For our calculations, we took the smallest observed dephasing rate.

**C. CW ODMR**

The data in subsection [III A] clearly show that 1-, 2-, and 3-photon transitions show different dependence on the RF power. It is therefore essential to model the system dynamics under different RF power levels and in constant laser light. To obtain the CW ODMR spectra, we integrated the master equation with the total Hamiltonian \( \mathcal{H}_R(t) = \mathcal{H} + \mathcal{H}_RF(t) \) for 4 µs and plotted the resulting signal as a function of the RF frequency. The ODMR signal was calculated as the difference \( S_{RF} - S_0 \) between the signal \( S_{RF} \) with applied RF field and the reference signal \( S_0 \). Each part was calculated from the diagonal elements of the stationary density matrix as \( S_{RF} = \rho_{11} - \rho_{22} - \rho_{33} + \rho_{44} \) [29], where \( \rho_{11}, \rho_{44} \) and \( \rho_{22}, \rho_{33} \) are the populations of the spin levels \( |\pm 3/2\rangle \) and \( |\pm 1/2\rangle \), respectively.

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V. ODMR IN A MAGNETIC FIELD

While the experiments described in the preceding sections were performed in zero field, we now consider the effect of magnetic fields. In subsection VA, we consider fields applied parallel to the symmetry axis of the center lifts the degeneracy of the energy levels as well as the transitions. This is particularly relevant as it allows one to distinguish between single- (e.g. \( +1/2 \leftrightarrow +3/2 \)) and multiple quantum transitions (e.g. \( -1/2 \leftrightarrow +3/2 \)) that are degenerate in zero field but behave differently. In subsection VB we also consider fields not aligned with the symmetry axis, which modify not only the transition frequencies but also the transition probabilities.

Figure 10 (a) and (b) shows the energy levels of \( V_2 \) and \( V_3 \) types of vacancies in an external magnetic field parallel to the crystal c-axis along with different types (multiple photon / multiple quantum observe in the experiment) transitions. The red arrows labeled with \( \nu_1 \) and \( \nu_2 \) represent the allowed single-quantum transition from \( |3/2 \rangle \leftrightarrow |1/2 \rangle \) and \( |-3/2 \rangle \leftrightarrow |-1/2 \rangle \), respectively. The blue arrows labeled with \( \nu_3 \) and \( \nu_4 \) represent the two-quantum transitions from \( |3/2 \rangle \leftrightarrow |-1/2 \rangle \) and \( |-3/2 \rangle \leftrightarrow |1/2 \rangle \), respectively.

In APPENDIX C, Fig. 15 shows different possible transitions for the \( V_1/V_3 \) and \( V_2 \) for a range of magnetic fields.

\[ \beta \approx 2.5 \, \mu s^{-1} (1.3 \, \mu s^{-1}) \] for \( V_2/V_3 \) to optimise the resolution. The pumping rate \( \delta = 1.4 \, ms^{-1} (6.8 \, ms^{-1}) \) for \( V_2/V_3 \) was extracted from the time-dependence of the PL signal measured after an RF pulse of 20 \( \mu s \) using the model described in Ref. [9]. Figure 9 (b) shows the ODMR signal for the 1-, 2-, and 3-RF photon peaks vs. the RF field strength \( \Omega_1 \). In the simulated ODMR spectra of the \( V_2 \) and \( V_3 \) vacancies, the 1-, 2-, and 3-RF photons absorption peaks are visible. The intensity of peak \( P_3 \) (3-RF photon transition) is small relative to other two peaks as compared to the experimental recorded spectra and we will address this in Sec. V C.

![Energy levels of (a) the \( V_2 \) vacancy and (b) \( V_3 \) vacancy in a magnetic field parallel to the crystal c-axis. Arrows represent the possible transitions. Red and blue arrows are for the one-photon transitions; green and yellow arrows are for the two-photon transitions; and black arrows are for the three-photon transitions.](image)

![Energy levels of (a) the \( V_2 \) vacancy and (b) \( V_3 \) vacancy in a magnetic field parallel to the crystal c-axis. Arrows represent the possible transitions. Red and blue arrows are for the one-photon transitions; green and yellow arrows are for the two-photon transitions; and black arrows are for the three-photon transitions.](image)

TABLE III. Detail of Figure 11 peak labels and their correspondence to the spin transition levels. \( \Delta m_x \) and \( \Delta \hbar \) are the changes in spin angular momentum and the number of absorbed RF photons for each transition and \( m = (g \mu_B B) \).
the spin levels $3/2 \leftrightarrow 1/2 (-3/2 \leftrightarrow -1/2)$ (as shown in Fig 11 (a) and (b) with three black arrows) and appears at one third of the corresponding transition frequency. Peaks labeled with 1 and 2 in Fig. 1 are 3 RF photons transition between $3/2 \leftrightarrow 1/2$ and $-3/2 \leftrightarrow -1/2$ of $V_3$. The slope of 2- and 3-photon transition between the levels $\pm 3/2 \leftrightarrow \mp 1/2$ is 2 and 3 times higher than the slope of the 1-photon transition. Additional peaks $d_{i=2,3}^b$ for $V_{i=2,3}$ type of $V_{Si}$' are due to the absorption of 1 RF photon by spin levels $\pm 3/2 \leftrightarrow \mp 1/2$. This type of transitions were also seen previously for the $V_2$ type of vacancies in $4H$-SiC, and the authors suggested that the cause of these transitions was the fine structure of the $V_2$ vacancy [22, 30]. Details of these peaks are given in Table III. Figure 11 (b) shows the corresponding simulated spectra for an external magnetic field almost parallel (angle of inclination is 2.5°) to the $c$-axis, obtained by numerically solving Eq. (7) using the same method and relaxation and pumping parameters are given in the above subsection III A. The applied magnetic field removes the degeneracies in the spin levels. For some magnetic field values, level-anticrossing also happens, so the reference signal $S_0$ was calculated from the diagonal elements of the stationary density matrix without RF for a particular magnetic field. The obtained ODMR signal was renormalized to match the experimental signal and plotted. The RF Strength $\Omega_1$ used for both vacancies was 6 MHz. In the simulations, 1- and 2- photon peaks are visible along with the 1 RF photon absorption peaks $d_{i=2,3}^b$ by spin levels $\pm 3/2 \leftrightarrow \mp 1/2$ of $V_{i=2,3}$ type of $V_{Si}$.

### B. Magnetic field with component perpendicular to the $c$-axis

The simulated ODMR of magnetic field small with $c$-axis enables the double quantum transitions $d_{i=2,3}^{b}$. It is interesting to see the effect of $B$ perpendicular to the $c$-axis. Figure 12 (a) shows the ODMR recorded in different magnetic fields $\perp$ to the $c$-axis in addition to a 9 mT magnetic field parallel to the $c$-axis at room temperature. With increasing magnetic field strength perpendicular to the $c$-axis, the signal amplitude of the peak $P_3^{1b}$ (due to spin transition $3/2 \leftrightarrow 1/2$) falls rapidly compared to the peak $P_3^{1b}$ (due to the spin transition $-3/2 \leftrightarrow -1/2$). At around 4.7 mT, the signal amplitude of the peak $P_3^{1a}$ is almost zero, but the signal for $P_3^{1b}$ remains. With further increase of the perpendicular magnetic field strength $P_3^{1b}$ amplitude becomes negative. The intensity pattern of the multi-photon peaks is also similar to peaks $P_3^{1a(b)}$. Figure 12 (b) shows the simulated ODMR recorded in different magnetic fields $\perp$ to the $c$-axis along with 9 mT magnetic field parallel to the $c$-axis. The RF strength $\Omega_1$ used for both vacancies was 2 MHz. In the simulations, we did not consider the effect of the magnetic field on the excited and shelving states of the silicon-vacancy, which can change the optical pumping scheme. Instead of equally populating ground state spin levels $\pm 1/2$, the spin level -1/2 gets slightly more populated; this could be the reason for the difference between the simulated and experimental intensity variation of peaks $P_3^{1b}$ and $P_2^{1b}$ with perpendicular magnetic.

### C. RF field with a component parallel to the $c$-axis

In the CW-ODMR experiments, we generate the RF field with a wire terminated by a 50 W attenuator with 50 $\Omega$ resistance. The resulting RF Hamiltonian includes a component of the magnetic field parallel to the $z$-axis ($c$-axis), which is usually ignored due to its negligible effect on 1 RF photon absorption transitions. However, with the relatively strong fields considered here, its effect can not be neglected, as we show here. Figure 13 (a) shows the experimental and simulated CW-ODMR spectra for $V_3$. The method used to simulate these plots is the same as explained in the above Sec. IV C except the Hamiltonian used is

$$H_{RF}(t) = \Omega_1 \cos(2\pi \omega t) (S_x + pS_z),$$

Eq. (8)
where $\Omega_1 = 4.7$ MHz and $0< p \leq 1$. The simulated spectra were also renormalized to match the experimental signal. The ODMR spectrum simulated with $p = 1$ matches well with experimentally measured spectrum. Figure 13 (b) compares experimental and simulated amplitudes of the different peaks vs. RF field strength. Dotted, dashed and solid curves are the simulations obtained by solving Eq. (7) numerically for different photons transitions with RF Hamiltonian given Eq. (5) with $p = 0, = 1,$ and $= 1$ along with consideration of the RF inhomogeneity, respectively. To account for the experimental RF inhomogeneity, signals with 0.5, 1 and 1.5 times $\Omega_1$, were calculated and added with weights 0.33, 0.34 and 0.33, respectively. We plot the experimental and simulated data in the same plot using $\Omega_1 = \kappa \sqrt{RF \text{ POWER}}$ with $\kappa = 0.25$ for 1-photon and $\approx 1$ for 2- and 3-photon transitions. Figure 13 (b) shows that the z-axis RF field strongly affects 2- and 3- RF photons absorption signals, but its effect on 1- RF photons absorption peak is negligible. The experimental data for amplitudes of the different peaks vs. RF field strength matches with the solid simulated curves, which also account for the inhomogeneity of the RF field.

VI. DISCUSSION AND CONCLUSION

$V_{Si}$ in SiC is optically addressable and stores information that can be manipulated using RF coherent control pulses. We studied the silicon vacancies by applying the high-power RF pulses. In the CW-ODMR experiments, we fitted the ODMR signal of 1, 2 and 3 RF photons with the square root of the RF power. We applied the maximum possible RF power with the RF amplifier and saturated the 1, 2 and 3 RF photons peaks of the $V_{Si}$ type of vacancy. But for the $V_{Si}$ kind of vacancy, we can only saturate the 1 RF photon absorption peak. The 1, 2 and 3 RF photons absorption peaks fitted well in Eq. 3 with the $c$ value is $\approx 1, 2$ and 3. The simulated ODMR Spectra and ODMR signal vs. RF coupling strengths show similar dependence.

We measured the Rabi oscillations of $V_{Si}$ type for the 1, 2, and 3 RF photon transitions, which fit well with RF coupling strength $\Omega = 9.1$ MHZ for all oscillations, but the dephasing rates differed. The 1 RF photon absorption transition dephase faster than 2 RF photons absorption transition and 2 RF photons absorption transition dephase faster than the 3 RF photons for the same RF power. It can be seen from the CW-ODMR also that the linewidth of 2 RF photons absorption transitions is smaller than the 1 RF photon absorption transitions. We saw very sharp changes in the 3 RF photons absorption Rabi oscillation simulations, but we did not see it in the experiment due to RF inhomogeneity. Further, the simulations of the population dynamics with the $\sigma^-$ polarized RF field show that the three spin levels -3/2, 1/2, and -1/2 were involved in the 2 and 3 RF photons absorption transitions. The populations of spin levels -3/2 and 1/2 were exchanging in 2 RF photons transitions, and for the 3 RF photons transitions, population exchange was between the spin levels -3/2, 1/2, and -1/2. With linearly polarized photons, the entire population flip happens between the spin levels only with 1-photon absorption and for the 2- and 3-photon it is RF strength depended. We successfully measured the FID of the $V_3$ type by exciting it with 1, 2, and 3 RF photons.

The magnetic field lifts the degeneracy in the vacancy spin levels, and we can see ODMR peaks for the different transitions. The ODMR recorded in the magnetic field parallel to the c-axis clearly shows these different RF photons transitions. The 1 RF photon absorption is transition takes place between the spin levels $\pm 3/2 \leftrightarrow \pm 1/2$ (with high ODMR intensity) and $\mp 3/2 \leftrightarrow \pm 1/2$ (with low ODMR intensity). The 2 RF photons transitions are taking place between the $\mp 3/2 \leftrightarrow \pm 1/2$ and with very low ODMR intensity in spin levels $\pm 3/2 \leftrightarrow \pm 1/2$ also. In the transition $\pm 3/2 \leftrightarrow \pm 1/2$ angular momentum change is $\pm 2$, so angular momentum is conserved for this transition with two RF photons of the same polarization, wherein the other is $\pm 1$, and it is not conserved, giving low intensity. The 3 RF photons absorption transition is taking place between the $\mp 3/2 \leftrightarrow \pm 1/2$. The intensity of these 3 RF photons absorption peaks ($P_{3a}$ and $P_{3b}$) is higher than that of the 2 RF photons absorption peaks ($P_{2a}$ and $P_{2b}$), i.e., transitions between the spin levels $\pm 3/2 \leftrightarrow \pm 1/2$. The higher intensity in 3 RF photons transitions is due to angular momentum conservation, and this could be possible if two out of three RF photons have the same polarization. The ODMR recorded in 9 mT parallel to the c-axis and along with the magnetic field perpendicular to the c-axis shows the perpendicular magnetic field mixing more the transition $-3/2 \leftrightarrow +1/2$ as compared to the $3/2 \leftrightarrow 1/2$. This effect could be use to prepare a pseudo pure state of $V_{Si}$ spin ensemble. Further, the multi-photon transitions depend not only on the amplitude but also on the orientation of the RF field with respect to the symmetry axis of the center.

So, in conclusion, 1, 2 and 3 photons transitions in the negatively charged silicon-vacancy have been observed and characterized. Our results improve the understanding of multi-photon absorption transitions in silicon vacancies and help develop fast quantum coherent control and other applications.

APPENDIX A: SAMPLE

SiC crystals with a low content of background impurities were grown from a synthesized source. Polycrystalline sources were synthesized from semiconductor silicon and spectrally pure carbon. Polycrystalline silicon and spectrally pure graphite in the form of powder were chosen as the powder. Before the synthesis, the crucible and internal furnace reinforcement were degassed at a temperature of 2200°C and a vacuum of $10^{-3}$ torrs for 2 hours by resistive heating growth machine, after which
FIG. 14. Experimental setup used for the ODMR experiments. An acoustic-optical modulator (labeled AOM) is used to generate laser light pulses. Mirror, lenses, iris and 850 nm long-pass filter are labeled M, L1, I, and F. An avalanche photodiode (APD) converts the PL signal into an electrical signal. Three orthogonal sets of Helmholtz coils labeled Cx, Cy and Cz are used to apply a magnetic field in an arbitrary direction.

APPENDIX B: ODMR SETUP

Figure 14 shows the setup used for the cw- and time-resolved ODMR measurements, which is also used in our previous work [9, 10]. We used a 785 nm diode laser as our light source (A laser diode (Thorlabs LD785-SE400), a laser diode controller (LDC202C series) and a temperature controller (TED 200C)). An acousto-optical modulator (NEC model OD8813A) was used for creating the laser light pulses. For applying the static magnetic field to the sample, we used three orthogonal coil-pairs. The PL signal was recorded with an avalanche photodiode (APD) module (C12703 series from Hamamatsu). The signal from the APD was recorded with the USB oscilloscope card (PicoScope 2000 series) during pulse mode ODMR experiments. For cw-ODMR, the signal from APD was recorded with the lock-in (SRS model SR830 DSP). An RF source, we used a direct digital synthesizer (DDS) AD9915 from Analog Devices. An RF signal from the source was amplified using an RF amplifier (LZY-22+ from mini circuits and ZHL-5W-1+). This amplified RF power feed to the sample with a 50 µm diameter wire terminated with a 50-ohm resistor via a 50 W attenuator. For pulsed ODMR experiments, we used an arbitrary wave generator (AWG) (DAx14000 from Hunter Micro). An RF signal from the source was amplified using an RF amplifier (LZY-22+ from mini circuits). This amplified RF power was applied to the sample with a Helmholtz-pair of RF coils with a diameter of 2.5 mm terminated with a 50-ohm resistor. We used a digital word generator (DWG; SpinCore PulseBlaster ESR-PRO PCI card) to generate TTL (transistor transistor logic) pulses that trigger the laser RF pulses.

APPENDIX C: LINDBLAD OPERATORS

Lindblad operators used in the Lindblad equation Eq. 7 for including the optical pumping process of the V3 type of vacancy:

\[
L_1 = \sqrt{\delta} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad L_2 = \sqrt{\delta} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix},
\]

\[
L_3 = \sqrt{\delta} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}, \quad L_4 = \sqrt{\delta} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix},
\]

Lindblad operators used for including the optical pumping process of the V2 type of vacancy:

\[
L_1 = \sqrt{\delta} \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}, \quad L_2 = \sqrt{\delta} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix},
\]

\[
L_3 = \sqrt{\delta} \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{pmatrix}, \quad L_4 = \sqrt{\delta} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix},
\]

\[
L_5 = \sqrt{\delta} \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}.
\]

Lindblad operators for including the relaxation contribution \( L_6 = \sqrt{2\gamma} S_z \), \( L_7 = \sqrt{2\alpha} S_x \), where \( S_z = \)
1/2 \begin{pmatrix}
3 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & -1 & 0 \\
0 & 0 & 0 & -3
\end{pmatrix}
and 
S_x = \frac{1}{2} \begin{pmatrix}
0 & \sqrt{3} & 0 & 0 \\
\sqrt{3} & 0 & 2 & 0 \\
0 & 2 & 0 & \sqrt{3} \\
0 & 0 & \sqrt{3} & 0
\end{pmatrix}.

The values of $k_i$ are used to solve Eq. 7 with the Runge-Kutta 4 method.

- $k_3 = -i(H(t_n)\rho(n) - \rho(n)H(t_n)) + \sum_{\alpha,\beta,\delta} L_i^\alpha . \rho(n) . L_i^\beta . \rho(n) . L_i^\delta . \rho(n) . L_i^\gamma . \rho(n)$;

- $k_2 = -i(H(t_{\frac{n}{2}} + t_n)(\Delta t_k + \rho_n) H(t_{\frac{n}{2}} + t_n) + \sum_{\alpha,\beta,\delta} L_i^\alpha . (\Delta t_k + \rho_n) . L_i^\beta . (\Delta t_k + \rho_n) . L_i^\gamma . (\Delta t_k + \rho_n))$;

- $k_1 = -i(H(t_{\frac{n}{2}} + t_n)(\Delta t_k + \rho_n) H(t_{\frac{n}{2}} + t_n) + \sum_{\alpha,\beta,\delta} L_i^\alpha . (\Delta t_k + \rho_n) . L_i^\beta . (\Delta t_k + \rho_n) . L_i^\gamma . (\Delta t_k + \rho_n))$.

Figure 15 shows different possible transitions for the $V_1/V_2$ for a range of magnetic fields $B || c$ axis, calculated using eigenvalues of Hamiltonian given in Eq. 6. Red and blue color lines represent the possible 1-, 2-, 3-RF photon absorption transitions.

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FIG. 15. Plot showing different possible transitions for the $V_1/V_3$ and $V_2$ for a range of magnetic fields $B \parallel c$ axis, calculated using eigenvalues of Hamiltonian given in Eq. (1). Peaks labeled with $P_1^a(b)$ ($P_3^a(b)$), $P_2^a(b)$ ($P_3^{2a}(b)$) and $P_3^{3a}(b)$ are 1, 2 and 3, RF photons absorption peaks due to the single quantum spin transition $\Delta m_s = 1$, where peaks $d_2^{a(b)}$ ($d_3^{a(b)}$) are 1 RF photon absorption peaks due to double quantum spin transition $\Delta m_s = 2$ for $V_2$ ($V_3$) type of $V_{Si}$. Slope of different transitions are depends on the number RF photon absorb $\Delta p$ and the change in the spin quantum number $\Delta m_s$ during the transitions.

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