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Vanadium in silicon carbide: telecom-ready spin centres with long relaxation lifetimes and hyperfine-resolved optical transitions

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Abstract

Vanadium in silicon carbide (SiC) is emerging as an important candidate system for quantum technology due to its optical transitions in the telecom wavelength range. However, several key characteristics of this defect family including their spin relaxation lifetime ($T_1$), charge state dynamics, and level structure are not fully understood. In this work, we determine the $T_1$ of an ensemble of vanadium defects, demonstrating that it can be greatly enhanced at low temperature. We observe a large spin contrast exceeding 90% and long spin-relaxation times of up to 25 s at 100 mK, and of order 1 s at 1.3 K. These measurements are complemented by a characterization of the ensemble charge state dynamics. The stable electron spin furthermore enables high-resolution characterization of the systems' hyperfine level structure via two-photon magneto-spectroscopy. The acquired insights point towards high-performance spin-photon interfaces based on vanadium in SiC.

1. Introduction

Semiconductor materials such as silicon (Si), diamond, and silicon carbide (SiC) are excellent hosts for defect centers given their large band gaps, hardness, and quiescent magnetic environment [1–3]. Numerous defects in these materials present transitions in the optical domain, coupled with long spin relaxation and coherence times [4–11]. These features make them attractive for applications in quantum sensing, computation, and communication [12]. However, most of these defects have optical transitions in the visible range, posing challenges for low-loss photonic systems and long-distance communication [13, 14].

For these reasons, spin centers emitting in the near infrared regime in Si [15–19] or SiC [20–23] have gained widespread interest in the community. These materials offer the additional advantage of enabling wafer scale processing and integration with semiconductor electronics and photonics. It has been shown that SiC has favorable properties which make it an attractive candidate to host solid-state spin qubits [12]. For example, silicon vacancy [24–26] and divacancy [27] centers are promising spin qubit candidates in SiC for which tremendous progress has been made [5, 6, 28–32]. In this work, we study the properties of neutral vanadium ($V^{4+}$) defect centers in the 4 H and 6 H polytypes of SiC between 100 mK and 2.5 K [33–35]. This transition metal defect offers bright and fast optical transitions in the telecom O-band around 1.3 μm, and is therefore highly suited for spin-photon entanglement and integration into ultralow-loss enhancement structures for long-range fiber based communication in silica optical fibers [14, 36–39]. The family of vanadium emitters has been investigated extensively as it is a common impurity, and has been used for decades in charge compensation for industrial wafer-grade SiC [35, 40]. Recent experiments have explored the properties of vanadium defects towards applications in quantum technology. Following a first assessment
of its luminescence properties and the theoretical description of the impurity in the SiC lattice, measurements on single defects revealed a highly stable and narrow photoluminescence excitation (PLE) spectrum, with spin dependent optical transitions and record narrow inhomogeneous linewidth distribution in isotopically purified material [36, 37, 41]. While first measurements of the spin properties of these defects were also undertaken, these experiments were performed at moderate cryogenic temperatures above 3 K, resulting in rather short spin lattice relaxation rates for the neutral vanadium in SiC. Many of the most important optical and spin properties for quantum applications, particularly those at low temperature, thus remain to be determined.

Here, we investigate several of these aspects in depth by performing all-optical spectroscopy, charge depletion, and spin relaxation measurements in the temperature regime below 2.5 K. Finally, two-laser spectroscopy of the defects enables detailed insight into the rich hyperfine level structure. These measurements lay the groundwork for methods enabling precise initialization and control of the electronic and nuclear spin degrees of freedom.

2. Optical spectroscopy of $^{51}\text{V}$ ensembles

The $^{51}\text{V}$ isotope substitutes a silicon atom as a dopant in the SiC lattice. Depending on the polytype of SiC, the vanadium atom can occupy inequivalent lattice sites. Here we focus on the neutral charge state of vanadium ($V^{4+}$) in the $\alpha$ sites of 4 H- and 6 H-SiC, with optical transitions at 1278.78 nm and 1308.56 nm. The electronic level structure of $V^{4+}$ is comparable to that of the group IV defects in diamond, such as the negative [42, 43] silicon vacancy center. This center, which also operates at temperatures below 1 K, is currently a leading platform for solid state quantum communication, although frequency conversion is necessary for long range links.

$V^{4+}$ has a single unpaired electron that is coupled to the nuclear spin of $^{51}\text{V}$. The center has two Kramers doublet ground states (GS1, GS2) and two optical excited states (ES1, ES2) [37]. The spin properties of these states can be described by a Hamiltonian in the following form, that includes Zeeman and hyperfine interaction terms:

$$H = \mu_B \mathbf{B} \cdot \mathbf{S} - \mu_N \mathbf{N} \mathbf{B} \cdot \mathbf{I} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}.$$  

Here $\mathbf{S}$ and $\mathbf{I}$ are the electronic ($S = 1/2$) and nuclear ($I = 7/2$) spin operators, $\mu_N$ and $\mathbf{g}$ are nuclear and effective electron $g$-factors, $\mathbf{B}$ is a static magnetic field and $\mathbf{A}$ is the hyperfine interaction tensor between the nuclear and effective electron spins. Both ground and excited states can be described with this Hamiltonian, but differ in their hyperfine interaction tensor and electron $g$-factor. In table 1 the parameters of the Hamiltonian for the $\alpha$ sites in both polytypes are displayed.

We first discuss resonant PLE measurements of the ensemble optical transition, performed using excitation with a tunable laser and collection of the photoluminescence emission from the subsequent decay. Stray counts from the excitation light are strongly suppressed by collecting only photons from the phonon sideband of the emission. We interface a vanadium ensemble in commercial grade wafers of 4 H-SiC or 6 H-SiC with a SMF-28 with a PC-ferrule end. The ferrule is spring loaded and aligned parallel to the wafer c-axis. Light reaching the sample is attenuated by 26–29 dB on its path from the tunable laser. Additionally, a superconducting solenoid is placed below the sample, to apply magnetic bias fields of up to 0.49 T along the c-axis. A schematic representation of the setup is shown in figure 1(a).

In our PLE spectroscopy data, recorded at a temperature of 100 mK and plotted in figure 1(b), we identify the GS1-ES1 transitions of the $\alpha$ sites in 4 H- and 6 H-SiC. The wavelengths of the transitions can be found in table 1 and are in agreement with previous studies [33, 37]. However, the lineshape and linewidth are strongly dependent on the crystal properties: Measurements on epitaxially grown samples [44] present a strongly asymmetric lineshape which is markedly narrower (see supplementary section II). Transitions involving the orbital states GS2 and ES2 were not observed. We attribute their absence to the thermal depopulation of the second ground state GS2 [33, 36, 37] and the orientation of the resonant illumination and collection of photons (the $k$-vector of the excitation light is parallel to the c-axis). Indeed, in accord with the crystal-field model proposed in reference [45], transitions from GS1 couple to ES1 via photons polarized perpendicular to the c-axis ($E \parallel c$), while the transition GS1 - ES2 requires $E \parallel c$ polarization of the incident light, which is not available in our experimental orientation. Similarly, decay from ES1 to GS2 cannot be efficiently detected in our geometry due to the dipole orientation [33, 45].

When a bias magnetic field of 0.49 T is applied, the luminescence decreases significantly. In order to understand this behavior, and to distinguish it from ionization effects, two further sets of PLE measurements were performed.

Charge holeburning: In high-power PLE measurements at 0 T, we observed a decay of the fluorescence signal in 4 H-$\alpha$ after prolonged exposure to resonant excitation. A bleaching experiment was therefore
### Table 1. System parameters.

| Name | 4 H-α | 6 H-α |
|------|-------|-------|
| ES1-GS1 | 1278.78 nm | 1308.56 nm |
| GS1: $g_{xx,yy}$, $g_{zz}$ (MHz) | 0, 1.748<sup>a</sup> | 0, 1.749<sup>a</sup> |
| GS1: $A_{xx,yy}$, $A_{zz}$ (MHz) | 165<sup>a</sup>, −165<sup>a</sup>, 232<sup>(5)</sup> | 165<sup>a</sup>, −165<sup>a</sup>, 232<sup>(5)</sup> |
| ES1: $g_{xx,yy}$, $g_{zz}$ (MHz) | −2.18(2) | −2.24<sup>a</sup> |
| ES1: $A_{xx}$, $A_{zz}$ (MHz) | 75<sup>(4)</sup>, −213<sup>(4)</sup> | 20<sup>a</sup>, 200(20)<sup>a</sup> |

<sup>a</sup>Values taken from literature [37, 46].

Figure 1. Optical spectroscopy of V<sup>4+</sup> ensembles in 4 H- and 6 H-SiC. (a) Experimental set-up: A SiC sample is mounted at the lowest stage of a dilution refrigerator operating at 100 mK. A superconducting solenoid with 4000 turns is located beneath the sample, and is used to generate DC magnetic fields of up to 0.49 T, parallel to the c-axis. The optical interface with the vanadium ensemble is a spring-loaded, commercial flat-polished (PC) fiber ferrule containing a single-mode fiber (SMF-28), positioned on the top surface of the sample and on axis with the solenoid. Resonant infrared and green (520 nm) laser light is transmitted through the fiber and illuminates the vanadium defects in the SiC sample. (b) Resonant PL spectroscopy with and without magnetic field for the $\alpha$—sites in 4 H- and 6 H-SiC. By tuning the laser through resonance we observe bright emission in the phonon sideband. Setting the bias magnetic field to 0.49 T results in a low amplitude in the spectroscopy signal. This effect is attributed to optical pumping of spin population into the opposite spin state, and thus out of resonance. The data traces are peak-normalized for clarity. The traces were collected without green excitation. (c) Charge holeburning. Driving the optical GS1-ES1 transition in 4 H-$\alpha$ continuously ionizes the defect. The PL signal drops over time and a spectral hole is formed at the wavelength of the driving laser. The hole width and depth are both dependent on the applied drive power. After bleaching, the hole persists over several hours at 100 mK. The power given in the figure refers to the laser output. (d) PL signal under continuous above band-gap illumination with a green laser at 0 T and 0.49 T magnetic field. The spectrum obtained with magnetic field is fitted with a sum of two copies of the zero-field lineshape with different amplitudes and frequency offsets, accounting for the two symmetrically Zeeman-shifted spin states and their relative populations (see text).

performed by tuning the excitation laser to the peak of the resonance and illuminating it for 60 s with different laser output powers. As can be seen in figure 1(c), a spectral hole at the laser frequency is formed. This hole persists for several hours and is due to ionization of resonant defects [47]. Both the width and the depth of the spectral hole increase with laser power, resulting in spectral holes with a width of 2 GHz to 6 GHz and a reduction in fluorescence by up to 80%. The width is far greater than the laser linewidth, which has a 400 kHz typical FWHM (full width at half maximum). Detailed information and plots of the hole burning experiments can be found in the supplementary materials III. Adding green illumination (520 nm) to the resonant excitation not only prevents bleaching, but increases the observed fluorescence count rate. In the experiment, we use this mechanism to restore the original spectrum without hole by reviving the ionized charges. Both the photo bleaching in 4 H and the absence of this effect in 6 H has been observed and is in agreement with previous work using this material [37]. However, we assume that the charge stability is highly dependent on the crystal quality and dopant concentration as, contrary to our measurements, photo bleaching has also been observed in 6 H [47]. These observations provide a basis for further investigations towards a complete understanding of the charge state dynamics of vanadium in 4 H- and 6 H-SiC. We underline that, even at the highest input power of 20 mW, charge bleaching occurs on a timescale of order
10 s. We have provided further details on the charge dynamics including a charge transition diagram in the supplementary materials under section III.

Spin depletion: Next, we discuss the PLE spectra of both defects with an applied magnetic field of 0.49 T, without green illumination. As can be seen in figure 1(b), application of a bias field results in a strong reduction of the fluorescence when compared to the zero field measurement. In contrast to the charge holeburning measurements, each frequency was only illuminated for 0.5 s at a laser output power of $-6$ dBm (250 µW), underlining that a different mechanism than charge depletion is at play. The different g-factors of ES1 and GS1 lead to a splitting between the optical transitions depending on the electron spin state due to the Zeeman effect. During the PLE sweep of the laser at high magnetic fields, the electrons can decay into the opposite spin state that is not resonant with the laser and thus no longer contribute to the fluorescence signal. This effect can be observed in both 4 H-α and 6 H-α, and leads to a reduction of the fluorescence signal of 90%. Under the assumption that the fluorescence is proportional to the population in the probed spin state, it is thereby depleted. We define this fluorescence reduction as the spin contrast. We underline that this depletion does not correspond to the polarization of the defect ensemble into a particular state.

Adding (low power) green illumination to the PLE measurement at a high magnetic field leads to a partial recovery of the fluorescence. This observation indicates that green illumination excites a wide range of transitions, promoting electrons to the conduction band and ionizing surrounding charge traps. These disruptive processes are likely to lead to the observed mixing of the spin states. The measured spectrum is therefore a result of spin mixing by the low power green illumination and simultaneous spin pumping by the resonant laser during the PLE sweep. The agreement of the measured spectrum with a fit using two copies of the lineshape obtained at zero field, each with different amplitudes, shifted symmetrically to account for the Zeeman effect, supports this interpretation. The observed imbalance between spin states corresponds to an effective spin temperature of $\sim 230$ mK, significantly higher than the cryostat temperature during this scan (170 mK). The green laser can therefore be used to initialize the spins in a mixed state. We use this mechanism for the spin lifetime measurements in the following section.

3. Electron spin lifetime

The electron spin lifetime of the ground state is an essential property for applications in quantum information and communication [48–51]. The spin lifetime needs to be sufficiently long for coherent spin manipulation, and hence sets a limit to the system’s viability as qubit or quantum memory. Spin in wide band gap crystals are promising in this respect, as other defects, for example the nitrogen vacancy center in diamond, show exceptionally long spin lifetimes [52].

We measure the spin relaxation for the 4 H-α and 6 H-α sites in the ground state at a magnetic field of 0.49 T. This field splits the spin states $|\text{GS}1\uparrow\rangle$ and $|\text{GS}1\downarrow\rangle$ by approximately 12 GHz. To extract information about the $T_1$ spin lifetime, we employ an all optical spin depletion recovery sequence with transient detection. First, we initialize the system in a mixed state with a green laser pulse. Next, we apply a short laser pulse ($\leq 1$ ms) resonant with the GS1-ES1 transition, which results in pumping of the population into the opposite electron spin state. During a variable wait time $\tau$, a fraction of the initial spin population recovers due to thermal relaxation. The recovered spin population is probed by a second resonant laser pulse.

In figure 2(a) we plot the time dependent spin population recovery for different temperatures in 4 H-α. The data is best described by a bi-exponential function with a fast ($\Gamma_0$) and slow ($\Gamma_1$) decay constant. A detailed definition of the fitted function is given in the supplementary materials under section V. The fast relaxation shows no temperature dependence below 1.7 K and has a constant rate $\Gamma_0$ of approximately 100 s$^{-1}$. We show that this decay can be eliminated by increasing the pump pulse length to 100 ms $\gg 1/\Gamma_0$ (figure 2(b)), hinting at a possible unknown shelving state within the system. The relaxation timescale of the mono-exponential recovery is in agreement with the slow decay rate $\Gamma_1$ determined using short initialization. We therefore identify the temperature dependent relaxation rate $\Gamma_1$ as the spin lattice relaxation rate in this temperature range, and find the slowest measured rate to be 0.041(1) s$^{-1}$ at around 100 mK (figure 2(c)), corresponding to a spin lifetime of 25(7) s. We note that all uncertainties given for the relaxation rates and lifetimes correspond to 95% confidence intervals ($2\sigma$). Increasing the temperature to 1.1 K results in a spin lifetime of about 1 s, which is fully sufficient for many of the intended applications. This temperature regime drastically reduces the cooling requirements, thus improving the prospects for practical implementation.

As the recovery in 6 H showed neither exponential nor bi-exponential, the measured 1/e value was used to extract a value for the spin relaxation rate. Further details can be found in the supplementary materials under section V B. For temperatures above 1 K the $1/e$ decay rate $\Gamma_1$ shows a similar temperature scaling as 4 H-α. However, in the low temperature limit, the decay rate decreases far more slowly, and is more than an order of magnitude larger than in 4 H. We measure the longest lifetime for the 6 H-α site of $\sim 1$ s at 150 mK.
Figure 2. Spin lifetime of vanadium in 4 H and 6H SiC. (a) Recovery signal obtained from a spin depletion and recovery sequence, shown above the plot, on 4 H-α at 0.49 T. First, the system is initialized in a mixed state with a 0.5 ms long green laser pulse (green rectangle), followed by pulse of 200 µs length, on resonance with the GS1-ES1 transition (red rectangle). This pulse probes the initial population and drives spins into the non-resonant spin state (dark state). After a variable wait time $\tau$, a readout pulse of the same length follows (red rectangle) and probes the recovered population in the initial spin state. This sequence is repeated for different wait times $\tau$ and sample temperatures. Error bars of the individual data points are within their marker size. The data for 4 H-α is fitted with a double exponential function from which the decay rates are extracted. (b) Recovery signal for 100 ms pump pulse at 1.3 K, compared to the 1.3 K data from panel (a). The double exponential is no longer apparent and the data is in agreement with a single exponential decay. For comparison the double exponential fit to the data from (a) is re-scaled and shown as a dashed line. The resulting decay constant for 100 ms initialization is in agreement with the value $\Gamma_1$ extracted from data recorded with 200 µs initialization. (c) Temperature dependence of the spin relaxation rate for 4 H-α and 6 H-α. Circles correspond to the α-site in 4 H-SiC and triangles to 6 H-SiC (for $T \leq 1.9$ K). In 4 H-SiC, two different time constants were extracted from the bi-exponential fit, one with a temperature independent decay rate ($\Gamma_0$) and one with a temperature dependent decay rate ($\Gamma_1$). The data traces marked with 4 H* (crosses) were recorded using a different setup (see text). The error in temperature is an upper bound which accounts for temperature fluctuations observed with a temperature sensor. (d) Depending on the strength of the magnetic field, the achievable spin depletion fraction varies and reaches a value of above 80% at 0.49 T. Each trace is fitted with a Lorentzian. All vertical error bars show the 95% confidence interval extracted from the fit to the data and arrows pointing downward indicate that these error bars extend below zero.

It was not possible to stabilize the temperature of the dilution refrigerator above 1.9 K. Data points at temperatures between 1.9 K and 2.5 K were therefore acquired in a helium flow cryostat on a second chip from the same 4 H-SiC wafer using time resolved absorption of a pulsed resonant driving laser at a comparable field of 0.44 T (see section V C in the supplementary). These measurements employed a lock-in scheme, providing a convenient method of averaging the weak photodiode signal. In this temperature range, the spin relaxation rates continue to increase with increasing temperature, reaching $\Gamma_0 = 1100(400)$ s$^{-1}$ and $\Gamma_1 = 10000(8000)$ s$^{-1}$ (see figure 2(c)). For 4 H-α below 1 K, the temperature dependence of $\Gamma_1$ is consistent with a direct relaxation process. We note that only a small subset of defects in the crystal is probed. The measured rate is therefore an upper bound on the true spin lattice relaxation rate, since this sub-ensemble could be subject to spin-spin interactions leading to spin diffusion [53–55]. Significant contributions of Orbach processes below 1 K are deemed highly unlikely given the comparatively large energies of the GS2 manifold and the first phononic mode [36, 37, 56]. At higher temperatures, our measurements indicate that two-phonon processes become dominant. However, the acquired data does not allow to precisely constrain the relaxation parameters, making it impossible to distinguish between Raman and Orbach processes in the temperature regime above 1 K. To determine the temperature dependence precisely will require significant further work, including detailed measurements in the temperature regime above 2 K. Similar conclusions can be reached for 6 H-α, though with far stronger relaxation at low temperatures.

Next, we measured the bias field dependence of the spin depletion for both defects between 0.03 T to 0.49 T. As the magnetic field decreases, we observe a strong decrease in the spin contrast. The dependence of
the spin depletion on the applied magnetic field for both 4 H-α and 6 H-α is shown in figure 2(d). This reduction of the spin depletion at low magnetic fields is likely due to spectral diffusion at magnetic fields where the electron Zeeman and hyperfine coupling are comparable [57, 58]. We fit a Lorentzian line to the data points and use equation (1) and g-factors in table 1 to obtain a linewidth of 0.6 GHz HWHM (half width at half maximum) in 6 H-SiC, measured at 0.15 K, and 0.8 GHz HWHM in 4 H-SiC, measured at 1.3 K. These values obtained from our ensemble measurements are moderately larger than what has been observed for a single vanadium spin in reference [37, 41]. We interpret these values as an upper limit for the single-spin spectral diffusion linewidths in this vanadium ensemble. The field dependence is compatible with the assumption that the depletion is due to a change in the spin state of the electron, since all of the dominant optical transitions of the defect are known to lie within the depletion linewidth, as discussed in the following section.

Finally, measurements were taken to characterize the magnetic field dependence of the spin lifetime for 4 H-α. Due to the strong reduction in the spin depletion contrast at low magnetic fields, a dependence of the relaxation rate on the magnetic field strength could not be resolved in the photoluminescence measurements at 1.3 K. At 2 K, the absorption measurement reveals a strong magnetic field dependence of the relaxation lifetime, which decreases by more than a factor of three when decreasing the bias field from 400 mT to 50 mT (see supplementary V E). This behavior is qualitatively consistent with what is expected from a two-level system [53]. However, due to the complexity of the multilevel ground state manifold, a quantitative comparison will require substantial further investigation.

4. Hyperfine structure

In order to better understand the observed shelving at high magnetic fields, further investigation into the magnetic field dependence of the optical transitions was conducted. Due to the inhomogeneously broadened transition [57] between the optical ground and excited state of the ensemble, it is challenging to extract information on the underlying hyperfine structure of the defect with single laser spectroscopy. With a second laser frequency, it is possible to address two transitions between the ground and excited state hyperfine manifolds simultaneously. This type of driving is only sensitive to the relative energy differences between the transitions which circumvents this limitation. We implement two-photon spectroscopy with a 5 GHz electro-optical modulator that is driven with two RF frequencies to create two sets of optical sidebands: one at a constant detuning of 4.5 GHz from the carrier, and a second set that can be swept from 3 GHz to 4.5 GHz. Placing the carrier outside of the inhomogeneous lineshape, excitation by the carrier as well as by the mirror sidebands and higher order harmonics is efficiently suppressed, resulting in an effective single-sideband excitation spectrum, but without the need for quadrature modulation or sideband filtering (see supplementary IV). This method thereby allows to detect transition pairs separated by the frequency difference between the two sidebands.

The method samples from the edge of the inhomogeneous distribution, for which strain, impurities, or isotopic effects may modify the local crystal field. This notwithstanding, no effects resulting from additional spins were resolved in the measurements, and there are no discernible shifts with respect to data taken near the peak of the distribution using singly-modulated excitation.

In figure 3(a) we show the observed PLE signal of the 4 H-α site as function of the two-photon detuning and applied bias magnetic field. 6 H-α exhibits very similar with the data set presented in the supplementary materials under IV A. We observe bright and dark features that can be mapped to different transitions by diagonalizing the Hamiltonian in equation (1). We categorize the observed features into four different subsets:

A transitions connect two different ground state levels via a common excited state. These transitions are visible as bright features, showing the ground state properties (figure 3(c)). Conversely, V-shaped transitions address two different excited-state levels from a common ground state (figure 3(d)). As the involved excited states can decay to off resonant ground state levels, the addressed ground state can be depleted, causing dark features in the observed fluorescence signal. The third category, displayed in figure 3(e), are V-like (V∗) or A-like (A∗) systems, but with different hyperfine states in the common electronic manifold. These features reveal information about both the ground and excited state manifold. At high magnetic fields, the Zeeman term in the Hamiltonian exceeds the hyperfine coupling, and spin conserving II transitions start to dominate the observed spectrum (figures 3(b) and (f)). Efficient optical excitation in this system is spin conserving [57, 59], but the excited states can decay via both spin-conserving and spin-flipping transitions. Following a spin flip, re-excitation occurs at the detuned frequency corresponding to the optical transition of the other spin state. The slope of these bright features as function of the magnetic field scales linearly with the difference between the ground and excited state electron g-factors (figure 3(h)). From the known gzz of GS1 we determine the excited state g-factor to be
Figure 3. Two-laser PLE spectroscopy data of 4 H-α. (a) The PLE signal is recorded as function of the external magnetic field ranging from 0 to 61 mT and the two laser detuning (0 to 1499 MHz) at a temperature $<1$ K. The plot is rich in bright and dark features, which we use to refine the hyperfine parameters of the excited state. (b) Extended-range two laser spectroscopy: The bright features correspond to Π transitions. These transitions are visible when the Zeeman energy outweighs the hyperfine interaction. The shaded field corresponds to the data range in (a). (c)–(f) By diagonalizing the Hamiltonian we are able to plot the relevant transitions and can categorize the features into different groups: The coloured/grey arrows denote the two laser energies, connecting different states of the ground state manifolds and excited state manifolds. $\Delta_g$ and $\Delta_e$ denote the splitting of the different spin states by the electronic Zeeman effect. (c) Λ transitions: The lasers address transitions from two different ground states to the same excited state, resulting in bright features. (d) V transitions: The two laser beams are resonant with transitions associated with a common ground state. Population is driven to two different excited states. From there, the population can decay to other, undriven states, depleting the common ground state and resulting in dark lines in the signal. The two excited states can be within the same or in two different excited state manifolds, $|e_\downarrow\rangle$ and $|e_\uparrow\rangle$. (e) Selected Λ* and V* transitions: Λ* and V-like systems are transition pairs that connect states in two different ground or excited state manifolds via two hyperfine states in a common excited or ground state electronic manifold, respectively. (f) Π (electron spin-conserving) transitions. Only transition pairs which connect states of the same nuclear spin at high field are shown.

g_{zz} = 2.18(2). X type transitions, which are electron spin flipping but nuclear spin conserving, are not clearly identifiable in the measured spectra. We have therefore not included them in our analysis. The salient features in the two-photon spectroscopy allow a refined determination of the excited-state hyperfine parameters: $A_{zz} = 75(4)$ MHz, $A_{xz} = -213(4)$ MHz (see table 1).

The large linewidths extracted from the field-dependent spin depletion measurements are broadly in agreement with previously measured, single-defect linewidths [37], but in stark contrast with the narrow features observed in figure 3. While the instantaneous linewidth of each defect may be narrow, laser illumination leads to a disturbance of the charge environment, and may cause spectral diffusion by shifting the resonance frequency via the Stark effect. This would have to be remedied for applications involving Purcell-enhanced photon emission, since the resulting inhomogeneous broadening will significantly reduce the performance of such a system [60]. However, laser-induced dynamics would not be of concern for schemes using interaction-free readout and entanglement, since these methods rely on negligible excitation of the system [61, 62].

5. Summary and conclusion

The low-temperature measurements of the vanadium α sites in 4 H-SiC and 6 H-SiC presented here further underscore the potential of these defects for applications in quantum photonics. The long spin relaxation lifetime observed at moderate field strengths ($0.1 \text{T} < B < 0.5 \text{T}$) for the α site in 4 H-SiC forms a strong basis for quantum memories and qubits, and provides ample time for entanglement distribution at the intercity scale without the need for optical frequency conversion. Given the advanced technological maturity of the 4 H-SiC material and the widespread availability of telecommunication hardware, for example wavelength division multiplexing components, around 1.28 µm, the α site in 4 H-SiC currently represents the most promising defect of this family for photonic quantum technologies.
Nonetheless, several effects observed herein require further investigation. Although the semi-insulating 4 H-SiC and 6 H-SiC samples are specified with the same background and vanadium dopant concentration, the charge state dynamics of the 4 H- and 6 H-α sites are significantly different. Hole burning was observed in 4 H, while the 6 H defect did not present any bleaching. Furthermore, the single-exponential spin relaxation of the 4 H site following enhanced initialization with long optical pulses was not reproduced in 6 H-α. The origin of these effects remains to be identified. Our measurements also indicate that the β defects are most likely not suitable for such applications, since their spin relaxation lifetimes are below 1 ms, as described in the supplementary materials.

The high spin contrast can be expected to improve even further when addressing a single defect, given the limitations of fiber illumination of a thick crystal slab. Together with the detailed understanding of the spin structure gained from the two-photon spectroscopy measurements, this mechanism provides a first step towards the initialization of the spin into a pure state within the ground state manifold [63]. Spectral diffusion, which likely is at the root of the reduced spin contrast at low magnetic field in this sample, may be mitigated by suppression of the charge carrier fluctuations in the vicinity of the vanadium defects [27]. Furthermore, the narrow features observed in the two-photon spectroscopy measurements make the vanadium α defects highly attractive for use in spin-photon interfaces.

Given the prospects provided in this study, the vanadium defects merit intense further study regarding their quantum properties, particularly their coherence lifetimes and the characteristics of single defects. Like erbium in silicon, vanadium offers direct telecom interfacing between spins and photons, albeit with a much faster optical transition [64, 65]. The similarities with the silicon vacancy in diamond suggest that the spin coherence lifetime of vanadium will also be sufficient to enable the storage of quantum information for long-distance communication, providing a clear perspective towards high-performance quantum networks [66–68].

Data availability statement
The datasets of this work are available from the corresponding authors upon reasonable request.

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Conflict of interest
The authors declare that they have no competing interests.

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