I. INTRODUCTION

Solid-state defects are attractive candidates for quantum technologies because they can have long spin coherence time and can be integrated into nanofabricated devices. However, interactions with phonons can lead to spin decoherence. Color centers in diamond with exceptionally long spin coherence time have been identified, such as the nitrogen-vacancy center (NV−), and these are promising candidates for a wide range of applications including quantum sensing [1], quantum information processing [2–5], and quantum networks [6–8]. More recently the negatively charged silicon vacancy center in diamond has been demonstrated to have better optical homogeneity but poor spin coherence at 4 K because of a phonon-mediated orbital relaxation process [9,10]. We recently demonstrated that the neutral state of the silicon vacancy center (SiV0) can be implanted with high conversion efficiency, it exhibits excellent optical coherence with more than 90% of its emission into a nearly transform-limited zero-phonon line which does not exhibit any spectral diffusion, and it displays long spin coherence times at temperatures up to 20 K [11]. These properties make it an ideal candidate for a single atom quantum memory in a quantum network. However, we also observed that at temperatures above 20 K both $T_1$ and $T_2$ decrease exponentially with temperature [11,12]. Understanding the origin of this process is crucial for extending the operation range of SiV0 to higher temperatures to enable new applications in quantum information processing and nanoscale sensing.

In this paper we investigate the spin-lattice relaxation of SiV0 in detail. The exponential temperature dependence of $T_1$ above 20 K is consistent with an Orbach process [13–15] with an activation energy ($E_a$) of 16.8 meV, and we observe that the relaxation rate has a sharp dependence on the angle ($\theta$) of the magnetic field ($\mathbf{B}$) relative to the symmetry axis of the defect [Fig. 1(a)]. As the angle of the magnetic field is rotated away from the crystallographic axis of SiV0 by just 5°, $T_1$ decreases by almost two orders of magnitude. $T_2$ follows the same temperature dependence but is drastically shorter than $T_1$. We propose that these observations result from phonon-mediated transitions to a low-lying excited state that are spin conserving when the magnetic field is aligned with the defect axis, and we discuss likely candidates for this excited state.

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FIG. 1. [(a), top] Ball and stick model of SiV⁰. Gray spheres are carbon atoms. The interstitial Si atom (blue sphere) and split vacancy (red spheres) are aligned along the ⟨111⟩ directions in the diamond lattice, and the magnetic field (B) forms angle θ with the defect axis. [(a), bottom] Ground-state SiV⁰ spin levels at B = 0. [(b), top] Ground-state spin levels at magnetic fields such that the Zeeman energy is high compared to the zero-field splitting (D). [(b), bottom] Magnetic-field dependence of spin levels with B || [111]. Arrows indicate the magnetic field required for each spin transition to match the 9.7 GHz resonator mode. (c) Pulsed electron cross-section (ESR) spectrum of SiV⁰ in D1 (circles) and D2 (squares) for two inequivalent orientations with B || [111]. Lines correspond to the best fit of Eq. (2).

II. METHODS

Two high-purity ⟨110⟩ diamonds grown by chemical vapor deposition were studied. The first diamond (D1) was doped during growth with boron (∼10¹⁷ cm⁻³) and silicon (∼10¹⁷ cm⁻³) and subsequently high-pressure–high-temperature annealed, resulting in a SiV⁰ concentration of 4 × 10¹⁶ cm⁻³ [18]. The silicon precursor was isotopically enriched with 90% ²⁸Si, and all measurements in D1 were conducted on a ²⁹Si hyperfine line. The second diamond (D2) was doped during growth with boron (∼10¹⁷ cm⁻³) and implanted with ²⁸Si (6.3 × 10¹⁵ cm⁻³) and was previously described in Ref. [11]. After implantation and annealing, the resulting SiV⁰ concentration was 5.1 × 10¹⁵ cm⁻³ within the implanted region. Pulsed X-band (9.7-GHz) ESR was performed in a dielectric volume resonator (Bruker MD5) with a quality factor of 5000 (see Appendix A) [19]. In all experiments the microwave power was chosen so that the excitation pulse bandwidth was greater than the bulk linewidth of spin transitions (∼1 MHz). T₂ was measured using a standard two-pulse Hahn echo sequence with an initial 100-ms green laser pulse (532 nm, 200 mW) to optically enhance the spin polarization. At 5 K, we achieve 11.5% optical spin polarization into m₁ = 0 [Fig. 1(c)]. T₁ was measured using a three-pulse inversion recovery sequence [20].

III. RESULTS

A. Temperature dependence of T₁ and T₂

The ground-state spin Hamiltonian is given by [18]

\[ \hat{H} = \hat{S} \cdot \hat{D} \hat{S} + \mu_B \hat{S} \cdot \hat{g} \hat{B}, \]

with electron spin S = 1, zero-field splitting tensor (D) with axial part Dₓ = 0.94 GHz (at T = 4.8 K), electron g tensor (g) with parallel and perpendicular components gₓ = 2.0042 and gᵧ = 2.0035, respectively, and the Bohr magneton μB. The D and g tensors are both aligned along the ⟨111⟩ directions. With the field aligned along [111], there are two inequivalent orientations [Fig. 1(c)]; one orientation aligned with the field, θ = 0° ([111], outer ESR peaks), and three equivalent orientations aligned off axis, θ = 109.5° ([111], [111], [111], inner ESR peaks).

We performed time-resolved measurements of spin relaxation and decoherence for both inequivalent orientations. At low temperatures, T₁ and T₂ are constant (Fig. 2). In sample D2, we previously reported that the SiV⁰ low-temperature T₂ is dominated by spectral diffusion from the 1.1% abundance of ¹³C nuclei, T₂ = 0.954 ± 0.025 ms [11]. By contrast, the SiV⁰ density in D1 is large enough that T₂ is limited by instantaneous diffusion, T₂ = 0.48 ± 0.03 ms (see Appendices B and C) [21]. At low temperatures, T₁ is constant, T₁ = 46 ± 2 s (D1), and T₁ = 45 ± 4 s (D2), similar to previous observations of NV⁻ [22].

Above 20 K, both T₁ and T₂ decrease exponentially with increasing temperature. In this regime the two inequivalent orientations exhibit similar T₂ but significantly different T₁’s, T₁ and T₂ exhibit the same Arrhenius slope (the slope of the logarithm of the rate vs inverse temperature) for both orientations. The data (T₁, [111], T₁, [111], T₂, [111], T₂, [111]) were
we propose a model that captures the four salient features of the data: (1) the strong anisotropy of $T_1$, (2) the biexponential nature of $T_1$, (3) the temperature dependence of $T_2$, and (4) the large ratio between $T_1$ and $T_2$. Generically, an Orbach process is a two-phonon process [15] that connects the ground-state spin sublevels $m_s = -1, 0, +1$ through an excited state ($\Psi$)) with amplitudes $t_{-1}$, $t_0$, and $t_{+1}$, respectively [Fig. 4(a)]. The amplitudes $t_{-1}$, $t_0$, and $t_{+1}$ are overlap parameters between the ground triplet states and the excited-state $m_s = \{m_s\} |\Psi\rangle$ (see Appendices G and H). This gives rise to three possible relaxation rates between pairs of ground-state spin sublevels $m_s \leftrightarrow m_{s'} = -1 \leftrightarrow 0$, $0 \leftrightarrow +1$, $-1 \leftrightarrow +1$, $\frac{1}{T_{1,m_s=m_{s'}}} = C |t_{m_s,m_{s'}}|^2 e^{-E_a/kT}$, (3) where $C$ is a constant. If the excited-state $\Psi$ is a singlet ($S = 0$), it is invariant under magnetic-field orientation, so the behavior of $T_1$ can be captured by considering the mixing of the ground state (see Appendix G). The mixing of the spin sublevels in the presence of a large off-axis magnetic field leads to

\[
\begin{pmatrix}
|t_{-1}|^2 \\
|t_0|^2 \\
|t_{+1}|^2
\end{pmatrix} = \begin{pmatrix}
\cos^2 \theta & \frac{1}{2} \sin^2 \theta & \sin^4 \frac{\theta}{2} \\
\frac{1}{2} \sin^2 \theta & \cos^2 \theta & \frac{1}{2} \sin^2 \theta \\
\sin^4 \frac{\theta}{2} & \frac{1}{2} \sin^2 \theta & \cos^4 \frac{\theta}{2}
\end{pmatrix}
\begin{pmatrix}
|t_{-1}^0|^2 \\
|t_0^0|^2 \\
|t_{+1}^0|^2
\end{pmatrix},
\]

where $|t_{m_s}^0|^2$ are the overlap parameters at zero magnetic field. Substituting Eq. (4) in Eq. (3) and solving the $3 \times 3$ relaxation rate matrix equation for the ground-state spin ($S = 1$) provides the $T_1$ relaxation times (see Appendix G). If $|t_0^0|^2 = |t_{-1}^0|^2 = |t_{+1}^0|^2$, then Eqs. (3) and (4) predict that the
spin relaxation is isotropic. However, if $|r_\pm|^2 \gg |r_0|^2$, $|r_\pm|^2$, the spin relaxation is strongly anisotropic with two characteristic times approximated as

$$\frac{1}{T_{1,a}} = \frac{3}{8} C |r_0|^4 \sin^2(\theta) e^{-E_a/kT},$$

$$\frac{1}{T_{1,b}} = \frac{1}{2} C |r_0|^4 \sin^2(\theta) e^{-E_a/kT}.$$ (5)

In this limit the model captures the observed angular dependence of the two timescales in $T_1$ [Fig. 3(a)]. By comparing numerical calculations of the orientation dependence of $T_1$ for different ratios of $|r_0|^2/|r_\pm|^2$ [Fig. 4(b)], we can place a lower bound on the imbalance between these rates $|r_0|^2/|r_\pm|^2 > 100$.

We can also predict the effect of this Orbach process on $T_2$. Customarily, the Orbach process is viewed as a spin-relaxation process [15]. However, phonon-mediated transitions to the excited state can also lead to decoherence even when the spin projection is preserved, similar to what has been observed for orbital relaxation in SiV$^-$ [16]. Although the spin-relaxation rate relies on a spin flip and therefore the product of the overlap parameters $\frac{1}{T} \propto |r_m|^2 |r_{m'}|^2$ [Fig. 4(a), left], the decoherence rate depends on the sum of overlap parameters $\frac{1}{T} \propto |r_m|^2 + |r_{m'}|^2$ [Fig. 4(a), right] if we assume the spin coherence is completely lost after a single excitation to the excited state $\Psi$. The angle-dependent ratio of $T_1$ to $T_2$ will therefore depend on the ratio of overlap parameters. The model predicts (Fig. 9)

$$\frac{T_{1,a}}{T_{2,0 \leftrightarrow \pm 1}} = \frac{(|r_{\pm}|^2 + |r_0|^2)(|r_0|^2 + 2|r_{\pm}|^2)}{3 |r_{\pm} r_0|^2}.$$ (6)

The orientation dependence of $T_2$ predicted from this model is plotted in Fig. 3(a) where we also included the effect of instantaneous diffusion in sample D1 and is plotted in detail in Fig. 11. The anisotropy in $T_2$ is mostly canceled in the sum $|r_m|^2 + |r_{m'}|^2$. The model provides the best fit for both the $T_1$ and the $T_2$ data when $|r_0|^2/|r_{\pm}|^2 \approx 125$ [Fig. 3(a)].

If excited-state $\Psi$ is instead a triplet ($S = 1$), the overlap parameters cannot be written compactly, but we analyze this case numerically (see Appendix H). Briefly, phonon-mediated orbital relaxation to a vibronic excited state is generally spin conserving, but differences in the ground- and excited-state spin Hamiltonians can lead to mixing during the time spent in the excited state. For SiV$^0$ the ground and excited states can have different zero-field splitting tensors ($D_e$ and $D_x$). Since the Zeeman splitting in these measurements is 9.7 GHz, the zero-field splittings must differ by a comparable scale in order to reproduce the observed ratio of $T_1$ to $T_2$, and we find that the data can be qualitatively reproduced when $D_e \sim 5–7$ GHz [Figs. 6 and 7(b)], compared to the ground-state zero-field splitting $D_x = 0.94$ GHz. It is unlikely that these splittings differ by such a large magnitude. Alternatively, the small ratio of $T_1$ to $T_2$ could also arise from incomplete spin dephasing. If the excited-state lifetime is short compared to the spin precession time ($\tau \ll \hbar/eE_{\text{Zeeman}} \sim 50$ ps), then the spin coherence is partially preserved through a single excitation to $\Psi$ [23]. A model involving a triplet excited state would therefore require either that $D_x \gg D_e$ or that the excited-state lifetime is short enough to partially preserve coherence.

IV. CONCLUSIONS

To summarize, we have shown that spin relaxation in SiV$^0$ at high temperatures is dominated by an Orbach process that is strongly dependent on the magnetic-field orientation and $T_2$ exhibits the same temperature dependence as $T_1$ but at a significantly faster rate. These observations can be explained by a model for the Orbach process where the overlap parameters from the $m_s = 0$ and $m_s = \pm 1$ spin sublevels to a singlet excited state are drastically different. We note that this is consistent with the preferential optical spin polarization through the intersystem crossing into $m_s = 0$ [Fig. 1(c)] [11]. Alternatively, these observations can be qualitatively reproduced by a model with a triplet excited state that either exhibits a much larger zero-field splitting than the ground state or a very short excited-state lifetime. Although our present results cannot definitively identify the excited state, detailed spectroscopy can help distinguish between these two cases. Absorption spectroscopy could elucidate the vibronic structure [24,25], and the nature of the singlet state can be explored using time-resolved photon correlation measurements and temperature-dependent intersystem crossing rates [26,27]. At temperatures well above the activation energy, there should be enough population in the excited state to observe spin-resonance transitions associated with a different zero-field splitting. We have not observed the existence of additional transitions, but on-going work includes increasing our sensitivity at higher temperatures to search for such states.

The strong intrinsic anisotropy in SiV$^0$ stands in contrast to prior studies of NV$^-$ in which spin relaxation is mostly insensitive to the magnetic-field orientation at low magnetic field (5 mT) [28]. Our work suggests that it would be interesting to perform measurements of the orientation
and temperature dependence of spin relaxation in NV$^-$ at high magnetic fields. Similarly, a more detailed orientation and temperature dependence of $T_{1,\text{spin}}$ in SiV$^-$ would further elucidate analogous spin- and orbital-relaxation processes, and recent measurements at dilution refrigerator temperatures have started to explore mechanisms for spin relaxation and decoherence [29,30].

These observations point to a particularly intriguing possibility for high-temperature operation if Ψ is a spin singlet. The small overlap parameters between $m_z = \pm 1$ and Ψ imply that superpositions of $m_z = \pm 1$ could have longer spin coherence time than even the measured single-quantum $T_1$ as they should be limited instead by the double-quantum $T_1$ (see Appendix J). Future experiments include double-quantum spin resonance to interrogate the coherence of such superposition states [31].

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Spin coherence measurements ($T_2$) were performed using a two-pulse Hahn echo sequence with an initial laser pulse to boost the echo strength by polarizing the spins preferentially into $m_z = 0$ [Fig. 5(b)]. Spin-relaxation measurements ($T_1$) were performed using a three-pulse inversion recovery sequence [Fig. 5(b)]. First a laser pulse is used to polarize the SiV$^0$ spins preferentially into $m_z = 0$. After a small delay to wait for any laser-induced noise to die out, a microwave π pulse is applied to invert the spin polarization even further away from the Boltzmann equilibrium. The waiting time in this inverted state ($T_1$) is varied, and a two-pulse Hahn echo sequence ($\pi/2 - \tau - \pi$ echo) is used to read out the polarization at the end of the waiting period. For the strongest signal $\tau$ is chosen to be much smaller than $T_2$.

APPENDIX A: EXPERIMENTAL DETAILS

Electron spin resonance was performed on a modified Bruker Elexys 580 system with a 1.4-T electromagnet [Fig. 5(a)]. This is performed by driving the TE011 mode of a cylindrical dielectric resonator (ER-4118X-MD5) (9.7 GHz) with an external vector microwave source (Agilent, E8267D). Temperature-dependent measurements were performed in an Oxford CF935 helium-flow cryostat. The microwave excitation channel consists of a vector microwave source (Agilent, E8267D), a variable gain solid-state amplifier (ARRA P4844-30). This allows for arbitrary waveform control as well as flexibility in the microwave power attenuation (ARRA P4844-30). This for sample D1 in Figs. 6, 10(c), and 11 [11].

The effect of instantaneous diffusion can be mitigated by using a smaller rotation angle ($\theta_2$) for the second microwave pulse of a Hahn echo sequence since the change in the net dipolar magnetic field scales as $\text{sins}^2(\theta_2)/2$. This results in a proportionally smaller phase accumulated by the central spin and a decoherence rate $1/T_2 \propto T_2^{-1} \text{sins}^2(\theta_2)/2$. Using a smaller rotating angle will enhance $T_2$, but it will also decrease the bulk echo signal by the same factor. In sample D1, the apparent decoherence rate increases linearly with $\text{sins}^2(\theta_2/2)$ (Fig. 6). The data were fit according to the following:

$$\frac{1}{T_2} = \frac{1}{T_{2(\text{SD})}} + \frac{1}{T_{2(\text{ID})}} \text{sins}^2(\theta_2/2),$$

where $T_{2(\text{SD})}$ is the spectral diffusion decay time. The fit results in $T_{2(\text{SD})} = 0.95 \pm 0.22$ ms, most likely arising from the 1.1% of the $^{13}$C nuclei [11] and $T_{2(\text{ID})} = 0.319 \pm 0.056$ ms.

We note that the Hahn echo spin coherence times reported for sample D1 in Figs. 6, 10(c), and 11 ($T_2 = 0.28$ ms) is not the same as the spin coherence time reported in Fig. 2 in the main text ($T_2 = 0.48$ ms). This arises from the nonuniform population distribution of SiV$^0$ centers in this sample over the four inequivalent crystal orientations ([111], [111], [111], [111]), which has been reported previously as sample C in Ref. [33]. The data in Figs. 3, 8, 10,
FIG. 5. (a) Electron spin-resonance setup. (b) Experimental pulse sequence for bulk electron spin-resonance measurements of $T_1$ and $T_2$. A vector microwave source is amplified and coupled capacitively to the TE011 mode of a sapphire-dielectric cylindrical resonator. The diamond sample sits in the center of the resonator where the microwave field ($B_{mw}$) is uniform. The spin echo is coupled out of the resonator through a different path set by a fast Hittite microwave switch and amplified by a low-noise cryogenic preamplifier. Optical excitation from a green laser (532 nm) is controlled with a mechanical shutter and fiber coupled to the sample.

11, and 6 are taken using the $[\bar{1}1\bar{1}]$ orientation (larger SiV$^0$ concentration), whereas the data in Fig. 2 are taken using the [111] orientation (smaller SiV$^0$ concentration).

APPENDIX C: DECOHERENCE ARISING FROM $T_1$-INDUCED SPIN FLIPS OF FAST RELAXING NEIGHBORS

An alternative hypothesis for the observed temperature dependence of $T_2$ (Fig. 2 in the main text) and its relative magnitude with respect to $T_1$ is that rapid dephasing arises from dipolar interactions with other SiV$^0$ spins in the bath, such as those misaligned with the external magnetic field. We can immediately rule out spectral diffusion from SiV$^0$ spin flip-flops and instantaneous diffusion mechanisms arising from dipolar interactions between SiV$^0$ centers since these mechanisms would be independent of temperature. Instead, we consider the contribution of spectral diffusion arising from the fast $T_1$ relaxation of nearby SiV$^0$ centers [34]. This decoherence mechanism is strongest when $T_1$ of the spin bath is comparable to $T_2$ of the central spin under consideration. In our samples, $T_2 \sim 0.5$ ms at low temperatures, which is comparable to $T_1 \sim 1$ ms of the three equivalent SiV$^0$ orientations misaligned with the magnetic field ($\theta \approx 109^\circ$) at temperatures above 20 K. We numerically model the contribution to the Hahn echo decay from these three equivalent off-axis sites for the range of densities in samples D1 and D2 [35]. The electron spin Hamiltonian describing a pair of SiV$^0$ spins $S_1$ and $S_2$ is given by

$$\hat{H} = \hbar \omega_1 \hat{S}_{1z} + \hbar \omega_2 \hat{S}_{2z} + \hbar A_{\perp z}(\theta) \hat{S}_{1z} \cdot \hat{S}_{2z} + \hat{V}_2(t),$$

(C1)
with dipolar interaction between the SiV⁰ spins,
\[ A(r_{12}) = g_1 g_2 \mu_B^2 \hbar^{-1} [1 - 3 \cos^2(\theta_{12})] r_{12}^{-3}, \]  
(C2)
where \( \omega_1 \) and \( \omega_2 \) are the transition frequencies of the spins, \( r_{12} \) is the distance between the spins, \( \theta_{12} \) is the angle between \( r_{12} \) and \( \mathbf{B} \), and \( g_1 \) and \( g_2 \) are the longitudinal components of the \( g \) tensors. For our model we consider that \( S_1 \) is a slow relaxing spin \((\theta = 0°)\) whose coherence time is being measured and \( S_2 \) is a fast relaxing spin \((\theta = 109°)\) whose spontaneous \( T_1 \) flips induce decoherence of \( S_1 \). The term \( V_2(\tau) \) accounts for the fast Orbach spin-relaxation rate of \( S_2 \) spins by inducing random spin flips at a rate \( W \). The contribution to the echo signal decay for \( S_1 \) is [35] as follows:
\[ V(2\tau) = \left[ \left( \cosh(R\tau) + \frac{W}{R} \sinh(R\tau) \right)^2 + \frac{A^2(r_{12})}{4R^2} \sinh(R\tau) \right] \exp(-2W\tau), \]  
(C3)
where \( \tau \) is the interpulse delay in a Hahn echo sequence, \( W = 1/T_1(\mathbf{I}) \) (fast relaxing sites, Fig. 7 blue line), \( R^2 = W^2 - A^2(r_{12}) / 4 \), and \( r_{12} = n^{-1/3} \) is the average interspin distance. This expression is averaged over all angles \( \theta_{12} \) and added to the Hahn echo decay that arises from \( ^{13}\text{C} \) spectral diffusion alone \( (T_{2,\text{SD}}) = 0.95 \text{ ms}) \). The resulting calculated Hahn echo decay times are shown in Fig. 7 for several SiV⁰ densities in and above the range of the two samples studied here, which have SiV⁰ concentrations of less than \( 5 \times 10^{16} \text{ cm}^{-3} \). The density required to account for the data would need to be 100 times higher. Furthermore, at high temperatures, motional narrowing should lead to an increase in \( T_2 \), which does not qualitatively agree with the observed temperature dependence (Figs. 2 and 7).

APPENDIX D: DYNAMICAL DECOUPLING USING THE CARR-PURCELL-MEIBOOM-GILL SEQUENCE

We previously reported dynamical decoupling measurements using the Carr-Purcell-Meiboom-Gill (CPMG) sequence on sample D2 [11,36]. The Hahn echo \( T_2 \) displays a plateau below 20 K corresponding to \(^{13}\text{C} \) spectral diffusion but is limited by an Orbach process above 20 K. We observed that \( T_{2,\text{CPMG}} \) is unchanged above 20 K and follows the temperature dependence of \( T_2 \). However, below 20 K \( T_{2,\text{CPMG}} \) becomes substantially longer than \( T_2 \) and follows the extrapolated temperature dependence of the Orbach process. We hypothesize that the CPMG experiment refocuses slow spectral diffusion that arises from the \(^{13}\text{C} \) nuclei, but it does not refocus fast effects from the Orbach process as expected. All of the points in the CPMG measurement lie along the same curve \( T_{2,\text{CPMG}} = A \exp(-E_a/kT) \), where \( A = 1180 \pm 210 \text{ kHz} \) and \( E_a = 16.8 \pm 1.5 \text{ meV} \) in the entire measured temperature range of 5–60 K.

APPENDIX E: ORIENTATION DEPENDENCE OF \( T_1 \) AND \( T_2 \) MEASURED ON \( m_z = -1 \leftrightarrow 0 \)

In the main text we presented the orientation dependence of the \( T_1 \) and \( T_2 \) times for SiV⁰ for measurements on the \( m_z = 0 \leftrightarrow +1 \) transition. We also repeated the same measurements on the \( m_z = -1 \leftrightarrow 0 \) transition and find that it gives a nearly identical orientation dependence (Fig. 8). Since \( T_{1, -1\leftrightarrow 0} \approx T_{1, 0\leftrightarrow 1} \), we can conclude that \( |r_{+1}^0| \approx |r_{-1}^0| \). Additionally, because of the 1-GHz zero-field splitting of SiV⁰, the measurements on the \( m_z = -1 \leftrightarrow 0 \) transition were performed at a field that was \( \approx 30 \text{ mT} \) larger (when aligned with the [111] direction) compared to the measurements on the \( m_z = 0 \leftrightarrow +1 \) transition in Fig. 3. This implies that the Orbach process has a weak dependence on the magnetic-field strength.

FIG. 7. Arrhenius plot of simulations of \( T_2 \) (red lines) resulting from spectral diffusion arising from fast relaxing SiV⁰ centers. The blue dashed line is a fit of Eq. (2) to the temperature dependence of \( T_1 \) (blue squares) of fast relaxing SiV⁰ sites. This fit is incorporated in Eq. (C3) to simulate \( T_2 \) for a range of defect densities (labels in units of \text{cm}^{-3} ). The simulations indicate that, for the range of densities studied, the decoherence arising from spin flips of nearby SiV⁰ centers is not significant and is inconsistent with the observed temperature dependence of \( T_2 \) (red dots).

FIG. 8. Orientation dependence of \( T_1 \) (blue) and \( T_2 \) (red) measured at 30 K on the \( m_z = -1 \leftrightarrow 0 \) transition. The lines were simulated for the Orbach model with a singlet excited state using Eq. (G12) and assuming \( |r_{+1}^0 / r_{+1}^z| = 125 \): (solid line) \( T_{1,\tau} \), (dashed line) \( T_{1,\phi} \), and (long dashed line) \( T_2 \).
overlap parameters at zero field. The analytical form of this relaxation of SiV₀ for an Orbach process mediated by a spin-Raman process is given by

\[ |3\bar{A}_{2g}^{m=0}⟩ = |3\bar{A}_{2g}^{m=0}⟩ + t_{0}^{0} |1E_{g}⟩, \]

\[ |3\bar{E}_{g}⟩ = |1E_{g}⟩ + \sum_{m_{s}} t_{m_{s}}^{0} |3A_{2g}^{m_{s}}⟩, \]  

where \( t_{m_{s}}^{0} \) are state mixing coefficients. In the main text we refer to them as overlap parameters that connect the singlet and triplet subspaces since \( t_{0}^{0} = \langle 3\bar{A}_{2g}^{m=0} | 1E_{g} \rangle \). The \( t_{m_{s}}^{0} \) coefficients arise from spin-orbit coupling and thus depend only on the orbital symmetry of the involved zero-field states, which is independent of the applied magnetic field.

The triplet eigenstates in the presence of a magnetic field can be found using a Wigner rotation to transform the eigenstates of the zero-field splitting term from the molecular frame to the laboratory frame (the frame in which the Zeeman interaction is diagonal). This model assumes that in a magnetic field the eigenstates of the spin Hamiltonian have mostly Zeeman character and the zero-field splitting term can be neglected. A general rotation \( R (\alpha, \beta, \gamma) \) can be expressed in terms of Euler angles,

\[ R (\alpha, \beta, \gamma) = R_{z}(\gamma) R_{y}(\beta) R_{x}(\alpha), \]

where \( \Omega = (\alpha, \beta, \gamma) \) is the set of Euler angles following the “passive” convention. Under this rotation the irreducible tensors in the spin Hamiltonian \( T_{J,m} \) transform to \( \rho_{J,m} \) as

\[ \rho_{J,m} = \sum_{m'} D_{m,m'}^{J}(\alpha, \beta, \gamma) T_{J,m'}, \]

where \( D_{m,m'}^{J}(\Omega) \) is the Wigner matrix of rank \( J \). The elements of this matrix are as follows:

\[ d_{m,m'}^{J}(\beta) = \int_{0,\phi} d\Omega Y_{Jm}(\theta, \phi) e^{-i\hbar (m'-m)J_{z}} Y_{Jm'}(\theta, \phi), \]

where \( Y_{Jm}(\theta, \phi) \)’s are the standard spherical harmonic functions and \( J_{z} \) is the component of the total angular momentum along \( \hat{n} \parallel \langle 110 \rangle \). Then for \( J = S = 1 \),

\[ \frac{1}{\sqrt{2}} \sin(\beta) e^{-i\alpha} \quad \frac{1}{\sqrt{2}} \cos(\beta) e^{-i(\alpha-\gamma)} \]

\[ \frac{1}{\sqrt{2}} \sin(\beta) e^{i\alpha} \quad -\frac{1}{\sqrt{2}} \sin(\beta) e^{i(\alpha+\gamma)}. \]

(averaging over \( \phi \)). The physical origin of the random-phase approximation can arise from taking an ensemble average over a bath of phonons that randomly induce transitions to the excited state through spin-orbit coupling. The result is as follows:

\[ |t_{m}|^{2} = \sum_{m} |D_{m,m}^{S=1}(\varphi, 0)|^{2} |t_{m}^{0}|^{2}, \]

FIG. 9. Plot of \( T_{1,a}/T_{1,b,\theta=1} \) vs \( |t_{0}^{0}|/|t_{2}^{0}| \) from Eqs. (5) and (6) for several values of \( \theta \).

APPENDIX F: RATIO OF \( T_{1} \) TO \( T_{2} \)

The singlet model predicts that the observed ratio of \( T_{1} \) to \( T_{2} \) in Figs. 2 and 3 is strongly dependent on the ratio of the overlap parameters at zero field. The analytical form of this dependence is shown in Eqs. (5) and (6) which is plotted in Fig. 9. This figure shows that this ratio is strongly dependent on the orientation of the magnetic field, indicating that the best way to extract the ratio of the zero-field overlap parameters is by performing a global fit across all orientations (Fig. 3).

APPENDIX G: MODEL FOR SPIN RELAXATION: ORBACH PROCESS WITH A SINGLET EXCITED STATE

Here we present a detailed analytical derivation of the spin relaxation of SiV₀ for an Orbach process mediated by a spin-singlet excited state. The neutral silicon vacancy center has \( D_{3d} \) symmetry with a ground spin-triplet state \( |3\bar{A}_{2g}⟩ \), and the first excited singlet state is expected to be \( |1E_{g}⟩ \). The splitting between these states is unknown. At zero magnetic field, the triplet and singlet states can mix through spin-orbit coupling assisted by phonons [37–40],

\[ |3\bar{A}_{2g}^{m=0}⟩ = |3\bar{A}_{2g}^{m=0}⟩ + t_{0}^{0} |1E_{g}⟩, \]

\[ |3\bar{A}_{2g}^{m=1}⟩ = |3\bar{A}_{2g}^{m=1}⟩ + t_{0}^{0} |1E_{g}⟩, \]

\[ |3\bar{E}_{g}⟩ = |1E_{g}⟩ + \sum_{m_{s}} t_{m_{s}}^{0} |3A_{2g}^{m_{s}}⟩, \]  

If we specifically define \( R \) as the rotation away from \( \langle 111 \rangle \) about the \( \langle 110 \rangle \) axis so that \( \alpha = \varphi, \beta = \theta, \) and \( \gamma = 0 \) define the orientation of the magnetic field, the mixing of the transition amplitudes is given by

\[ t_{m} = \sum_{m} D_{m',m}^{S=1}(\varphi, 0) t_{m}^{0}. \]

From this we obtain the transition rates (\( |t_{m}|^{2} \)) by invoking the random-phase approximation to neglect the cross terms.
where

\[
|D_{m,m'}(\varphi, \theta, 0)|^2 = \begin{pmatrix}
\cos^2(\theta/2) & \frac{1}{2} \sin^2(\theta) & \sin^4(\theta/2) \\
\frac{1}{2} \sin^2(\theta) & \cos^2(\theta) & \frac{1}{2} \sin^2(\theta) \\
\sin^4(\theta/2) & \frac{1}{2} \sin^2(\theta) & \cos^4(\theta/2)
\end{pmatrix}.
\]  

(G9)

In the main text, Eq. (3) for the overlap coefficients in the presence of an off-axis magnetic field is obtained by substituting Eq. (G9) into Eq. (G8).

Next, the transition rate matrix [Eq. (G9)] can be used to model the spin-relaxation processes for \( S = 1 \) where the populations \( P = (P_{-1}, P_0, P_{+1}) \) evolve according to

\[
\frac{dP(t)}{dt} = \dot{R}P(t),
\]

where the rate matrix \( \dot{R} \) is given by

\[
R_{m,m'} = C(1 - \delta_{m,m'}) \mu^{m-m'} |t_m|^2 |t_{m'}|^2
\]

\[ - C \delta_{m,m'} \left( \sum_{m \neq m'} |t_m|^2 |t_{m'}|^2 \mu^{m-m'} \right),
\]

(G11)

where \( \delta_{m,m'} \) is the Kronecker \( \delta \) function and \( \mu = \exp(hf/kT) \) is the Boltzmann factor at \( T = 30 \) K and \( f = 9.7 \) GHz. Assuming that \( |t_0|^2 = |t_\pm|^2 \) and \( \mu = 1(hf \ll kT) \), this results in two distinct rate eigenvalues \( \lambda_1 \) and \( \lambda_2 \) corresponding to \( T_{1,a} = \lambda_1 e^{-E_a/kT} \) and \( T_{1,b} = \lambda_2 e^{-E_a/kT} \).

\[
T_{1,a} = \frac{2e^{-E_a/kT}}{3C|t_0|^2(|t_+|^2 + |t_0|^2)},
\]

\[
T_{1,b} = \frac{e^{-E_a/kT}}{C(|t_-|^2(2|t_+|^2 + |t_0|^2))}.
\]

(G12)

Equations (G12) were used to simulate the angular dependence of \( T_1 \) as a function of \( |t_0|^2/|t_\pm|^2 \) in Figs. 3(a) and 4(b). If we assume that \( |t_0|^2 \gg |t_\pm|^2 \) then Eqs. (G12) reduce to Eqs. (5).

APPENDIX H: MODEL FOR SPIN RELAXATION:

ORBACH PROCESS WITH A TRIPLET EXCITED STATE

The excited state can also be a spin-triplet state, such as a quasilocalized vibronic mode or a low lying electronic state. For this model we define two \( S = 1 \) spin Hamiltonians for the ground state (\( \hat{H}_g \)) and excited state (\( \hat{H}_e \)) that differ only in their zero-field splitting tensors (\( \hat{D}_g \neq \hat{D}_e \)).

\[
\hat{H}_g = \hat{S}^g \hat{D}_g \hat{S} + \mu_B \hat{S}^g \hat{g} \hat{B} \quad \hat{H}_e = \hat{S}^e \hat{D}_e \hat{S} + \mu_B \hat{S}^e \hat{g} \hat{B},
\]

(H1)

with eigenstates \( |m_z \rangle \) and \( |n_z \rangle \), respectively. The rate matrix describing the spin relaxation is given by

\[
R_{m,m'} = C(1 - \delta_{m,m'}) \sum_n |g(m|n)\rangle \langle n|m'\rangle |^2 \mu^{m-m'}
\]

\[ - C \delta_{m,m'} \left( \sum_{m \neq m'} |g(m')|^2 \langle n|m')\rangle^2 \right).
\]

(H2)

FIG. 10. (a) Model for the Orbach process of SiV\(^0\) with a singlet excited state. The transition rates \( |t_{m,m'}|^2 \) are determined by spin-orbit coupling and depend on the overlap between the electronic wave functions of the ground triplet state and the excited singlet state. (b) Model for the Orbach process of SiV\(^0\) with a triplet excited state. The transition rates between the ground-state spin sublevels depend on the overlap between the spin eigenstates of the ground state and the excited state and must be summed over all spin sublevels in the excited state. (c) \( T_1 \) and \( T_2 \) orientation dependence from Fig. 3(a), plotted against calculated fits from the singlet (black) and triplet (red) Orbach models: \( T_{1,a} \) (solid line), \( T_{1,b} \) (dashed line), and \( T_{2} \) (long dashed line). The singlet model fit assumes \( |t_0|^2/|t_\pm|^2 = 125 \). The triplet model fit assumes a coaxial excited state ZFS tensor with \( D_e = 5 \) GHz.

In the triplet model spin flips can occur through any of the three spin sublevels of the excited state [Fig. 10(b)], increasing the complexity of the rate matrix. Spin relaxation arises from the overlap between the eigenstates of the two triplet states, and slight variations in the character of the states become important. Thus the zero-field splitting terms for both the ground state and the excited state cannot be neglected when calculating the triplet state overlap coefficients and the rate matrix \( R_{m,m'} \). For these reasons the analytical solution for
the Orbach model with a triplet excited state is not compact, and instead we numerically simulate the spin relaxation by diagonalizing the rate matrix Eq. (H2).

In general, $D_e$ can differ from $D_0$ in its quantization axis, its magnitude of the axial component, or its magnitude of the rhombicity parameter. In the case where the quantization axis of the excited state is not aligned with the quantization axis of the ground state (e.g., due to an $E$-type quasilocalized vibronic mode that breaks $D_{3d}$ symmetry), the resulting orientation dependence qualitatively disagrees with the $T_1$ data. The same disagreement was found to be true for the case where rhombicity was introduced into the excited-state data. The same disagreement was found to be true for the case where rhombicity was introduced into the excited-state data. The simulated fits according to the singlet [Fig. 11(a)] and triplet [Fig. 11(b)] models using the $r_0^0$, $r_0^1$, and $C$ parameters determined from the $T_1$ data. The singlet model has no other free-fitting parameters, and we plot Eq. (I1) for the singlet model assuming that $|r_0^0|/|r_0^1| = 125$ as determined from the fit of the $T_1$ orientation dependence [Fig. 3(a)]. The singlet model predicts the magnitude of $T_2$ with reasonable accuracy.

The triplet model has four free parameters, two angles that set the quantization axis of the excited state, the axial part of the zero-field splitting tensor, and the rhombic part of the zero-field splitting tensor. We only consider the case where the zero-field splitting tensor of the excited state is axial and aligned with the symmetry axis of the defect since this is the case that best produces the measured $T_1$ orientation dependence [Fig. 10(c)]. The dependence for several values of $D_e$ is shown, and the best fit occurs with $D_e \approx 5–7$ GHz. Alternatively, if the spin does not fully decohere through a single cycle through the excited states.

**APPENDIX I: ORIENTATION DEPENDENCE OF $T_2$**

Our model for the Orbach process predicts a weak orientation dependence of $T_2$. The orientation dependence fits shown in Fig. 3(a) utilize the same overlap amplitudes ($t_0^0$, $t_0^1$) to explain both $T_1$ and $T_2$. The actual expression used in fitting the $T_2$ dependence in Fig. 3(a) is given by

$$\frac{1}{T_{2,0\rightarrow \pm 1}} = \frac{1}{3} C (|t_0^0|^2 + 2|t_0^1|^2)(|t_0^0|^2 + |t_0^1|^2) + \frac{1}{T_{2(ID)}} + \frac{1}{T_{2(SD)}},$$

which in addition to the Orbach process also includes instantaneous diffusion and $^{13}$C spectral diffusion mechanisms. We used $T_{2(ID)} = 0.319$ and $T_{2(SD)} = 0.95$ ms in these simulations.

The orientation dependence of $T_2$ is shown in Fig. 11 with the simulated fits according to the singlet [Fig. 11(a)] and triplet [Fig. 11(b)] models using the $r_0^0$, and $C$ parameters determined from the $T_1$ data. The singlet model has no other free-fitting parameters, and we plot Eq. (I1) for the singlet model assuming that $|r_0^0|/|r_0^1| = 125$ as determined from the fit of the $T_1$ orientation dependence [Fig. 3(a)]. The singlet model predicts the magnitude of $T_2$ with reasonable accuracy.

The triplet model has four free parameters, two angles that set the quantization axis of the excited state, the axial part of the zero-field splitting tensor, and the rhombic part of the zero-field splitting tensor. We only consider the case where the zero-field splitting tensor of the excited state is axial and aligned with the symmetry axis of the defect since this is the case that best produces the measured $T_1$ orientation dependence [Fig. 10(c)]. The dependence for several values of $D_e$ is shown, and the best fit occurs with $D_e \approx 5–7$ GHz. Alternatively, if the spin does not fully decohere through a single cycle through the excited states.
state, the magnitude of $T_2$ can be larger than the simulated values.

**APPENDIX J: DOUBLE-QUANTUM COHERENCE TIME**

The Orbach process affects the double-quantum transition $(m_z = -1 \leftrightarrow +1)$ through the overlap parameters $t_{z+1}, t_{z-1}$, and from the anisotropy of $T_1$ (Fig. 3), we know that $|t_{z+1}^0|, |t_{z-1}^0| \ll |t_0^0|$. It follows that $\frac{1}{T_{z+1,0}} \propto |t_{z+1}^0| + |t_{z-1}^0| \ll |t_0^0|^2 + |t_0^0| = \frac{1}{T_{z+1,0}}$ so that the double-quantum coherence time should be longer at the zero field or with the magnetic field aligned along the defect axis. Moreover for small angles of the magnetic field the double-quantum coherence time can be longer than the single-quantum $T_1$ time, even when the single-quantum coherence time is much shorter (Fig. 12).

FIG. 12. Simulated orientation dependence of $T_1/T_2$ for the Orbach process at 30 K showing the $m_z = 0 \leftrightarrow +1$ (black curve) and $m_z = -1 \leftrightarrow +1$ (red curve) coherence times compared to $T_{z+1,0}$. The dashed blue mark lines where $T_1 = T_2$, and only the $m_z = -1 \leftrightarrow +1$ curve dips below this, achieving the condition $T_1/T_2 < 1$.


