Vibronic States and Their Effect on the Temperature and Strain Dependence of Silicon-Vacancy Qubits in 4H-SiC

Péter Udvarhelyi,^{1,2,3} Gergő Thiering^④,² Naoya Morioka^④,⁴ Charles Babin,⁴ Florian Kaiser,⁴ Daniil Lukin,⁵ Takeshi Ohshima^④,⁶ Jawad Ul-Hassan^④,⁷ Nguyen Tien Son^④,⁷ Jelena Vučković,⁵ Jörg Wrachtrup,⁴ and Adam Gali^{④2,3,*}

¹Department of Biological Physics, Eötvös University, Pázmány Péter sétány 1/A, Budapest, 1117, Hungary

²Wigner Research Centre for Physics, P.O. Box 49, Budapest, 1525, Hungary

³Department of Atomic Physics, Budapest University of Technology and Economics, Budafoki út 8, Budapest, 1111, Hungary

⁴3rd Institute of Physics, University of Stuttgart and Institute for Quantum Science and Technology IQST, 70569, Stuttgart, Germany

⁵E. L. Ginzton Laboratory, Stanford University, Stanford, California, USA

⁶National Institutes for Quantum and Radiological Science and Technology, Takasaki, Gunma, 370-1292, Japan

⁷Department of Physics, Chemistry and Biology, Linköping University, 58183 Linköping, Sweden

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Silicon-vacancy qubits in silicon carbide (SiC) are emerging tools in quantum-technology applications due to their excellent optical and spin properties. In this paper, we explore the effect of temperature and strain on these properties by focusing on the two silicon-vacancy qubits, V1 and V2, in 4H-SiC. We apply density-functional theory beyond the Born-Oppenheimer approximation to describe the temperature-dependent mixing of electronic excited states assisted by phonons. We obtain a polaronic gap of around 5 and 22 meV for the V1 and V2 centers, respectively, which results in a significant difference in the temperature-dependent dephasing and zero-field splitting of the excited states, which explains recent experimental findings. We also compute how crystal deformations affect the zero-phonon line of these emitters. Our predictions are important ingredients in any quantum applications of these qubits sensitive to these effects.

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I. INTRODUCTION

Deep-level paramagnetic point defects in solid-state hosts can be used for quantum-technology applications owing to their long-lived coherent spin state. In these applications, the quality of the optical properties is crucial. Additionally, these parameters are coupled to external perturbations such as changes in the strain and electromagnetic fields and temperature, either directly or elaborately mixed by spin-orbit and electron-phonon coupling. In this paper, we study these interactions in the negatively charged silicon-vacancy centers in 4H-SiC. These are emerging quantum defects with long spin coherence time at cryogenic temperatures and fluorescence in the near-infrared region [1–4]. The centers have C_{3v} symmetry and a spin quartet 4A_2 ground state [5–7]. They show an extremely robust zero-phonon line (ZPL) [8] from the excited 4A_2 state in the photoluminescence (PL) spectrum, labeled “V1” (1.438 eV) and “V2” (1.352 eV) for

h -site and k -site vacancy, respectively [9,10]. Another ZPL for h -site silicon vacancy was observed 5 meV higher in energy that was associated with the transition from the second excited state (4E) called “V1'” [6]. However, its counterpart for k -site silicon vacancy (V2') has not yet been observed. The ground-state and excited-state spin sublevels are split by the dipolar electron-spin–electron-spin interaction that is called “zero-field splitting” (ZFS). Because of Kramers degeneracy, only axial splitting with $2D$ is allowed between the $\pm\frac{1}{2}$ and $\pm\frac{3}{2}$ levels. The experimental values of the ZFS in the ground state are 5 and 70 MHz for V1 and V2 centers, respectively, which are relatively small values because of the small deviation from the quasitetrahedral symmetry of the spin density [11]. In striking contrast, the values are on the order of about 1 GHz in the excited state for both centers at cryogenic temperatures [8,12], with a strong temperature dependence for the V2 center between cryogenic temperature and room temperature [13].

In this paper, we explore the origin of the measured magneto-optical parameters and their temperature

*agali@eik.bme.hu

dependence with *ab initio* calculations and experimental data. We calculate the excited-state polaronic fine structure of V1 and V2 PL centers using advanced density-functional theory (DFT). We model the vibronic interactions between these states including a crystal-field strain as a perturbation. From these results, we identify V1' and V2' as polaronic excited states, in contrast with the previously assumed electronic excited states. We predict the magnitude of the ZFS in the excited state as a function of temperature. We also provide a model for the temperature-dependent PL linewidth of the centers on resonant excitation.

II. COMPUTATIONAL METHODS

We apply a screened hybrid density-functional theory, Heyd-Scuzeria-Ernzerhof HSE06 DFT [14,15], for the calculation of electronic states and structure relaxation as implemented in the plane-wave-based Vienna *ab initio* simulation package (VASP) [16–19]. This functional produces accurate ionization and excitation energies of point defects in group-IV semiconductors [20]. For the spin-orbit, vibrational, and strain calculations, we use the computationally-less-demanding-than-HSE06 but still-accurate Perdew-Burke-Ernzerhof functional [21]. We use a 420-eV plane-wave cutoff and the projector-augmented-wave formalism [22]. Strain calculations are performed with an increased plane-wave cutoff of 600 eV. The model of the silicon-vacancy center is embedded in a 768-atom supercell, which is sufficiently large to use Γ -point sampling of the Brillouin zone. We calculate the excited electronic structure using the Δ SCF method, which is based on constraint occupation of Kohn-Sham states [23]. For the calculation of ZFS parameters, we use the VASP projector-augmented-wave [24] implementation of dipolar electron spin-spin interaction as implemented by Martijn Marsman. The spin quantization axis in spin-orbit-coupling calculations is specified to be parallel with the symmetry axis of the defect.

III. SAMPLE PREPARATION

The 100- μm -thick $^{28}\text{Si}^{12}\text{C}$ -enriched 4H-SiC layer is grown by chemical vapor deposition on an *n*-type (0001) 4H-SiC substrate. The isotope purity is measured by secondary-ion mass spectroscopy and inferred to be approximately 99.85% for ^{28}Si and approximately 99.98% for ^{12}C . The thickness of the epitaxial layer is approximately 100 μm , and the surface is smoothened by chemical-mechanical polishing. Current-voltage measurements at room temperature show that the layer is *n* type with a free carrier concentration of approximately $6 \times 10^{13} \text{ cm}^{-3}$, which is close to the concentration of shallow nitrogen donors of approximately $3.5 \times 10^{13} \text{ cm}^{-3}$ determined from photoluminescence at low temperatures. Deep-level transient spectroscopy measurements show that

the dominant electron trap in the layer is related to the carbon vacancy with a concentration in the mid- 10^{12} cm^{-3} range. Minority-carrier-lifetime mapping of the carrier shows a homogeneous carrier lifetime of approximately 0.6 μs . We expect the real value to be twice as high, as an optical method with high injection is used [25]. Thus, the density of all electron traps should be limited to the mid- 10^{13} cm^{-3} range [26]. Individually addressable silicon-vacancy centers are created through room-temperature electron-beam irradiation at 2 MeV with a fluence of 10^{13} cm^{-2} . Some interstitial-related defects are removed by subsequent annealing at 300 °C for 30 min. The 4H-SiC sample used is flipped to the side (i.e. by 90° compared with the *c* axis) such that the polarization of the excitation lasers is parallel to the *c* axis ($E \parallel c$), which allows us to excite the V1 and V2 excited states with maximum efficiency.

To increase the efficiency of light extraction from the high-refractive-index material ($n \approx 2.6$), we fabricate a solid immersion lens using a focused-ion-beam-milling machine (Helios NanoLab 650). The related surface contamination and modifications are subsequently removed by peroxymonosulfuric acid treatment for 2 h.

A thin wire is placed next to the solid immersion lens to apply continuous radio-frequency waves to mix the spin ground states of silicon-vacancy centers. This suppresses optical spin pumping and allows permanent observation of resonant absorption lines.

IV. EXPERIMENTAL SETUP AND PROCEDURE

All the experiments are performed at cryogenic temperatures of 4–28 K in a Montana Instruments Cryostation. A homebuilt confocal microscope is used for optical excitation and subsequent fluorescence detection of single silicon vacancies. Initially, silicon-vacancy centers are identified via confocal microscopy and spectroscopy with use of continuous-wave off-resonant optical excitation at 730 nm. For resonant optical excitation at 862 nm (V1 center), we use an external-cavity tunable diode laser (Toptica DLC DL PRO 850). For resonant optical excitation at 916 nm (V2 center), we use a Ti:sapphire laser (Msquared Solstis). All measurements are referenced to a wavelength meter (High Finesse WS7-30) with about 30-MHz accuracy.

Laser light is focused onto the sample with a vacuum-compatible microscope objective (Zeiss EC Epiplan-Neofluar 100 $\times$, NA 0.9). The fluorescence is collected by the same microscope objective and separated from parasitic laser light by a dichroic mirror (Semrock Versa Chrome Edge). Phonon-sideband fluorescence is detected with a silicon single-photon-counting module (Excelitas SPCM-AQRH-W4 and SPCM-AQRH-14). To obtain a resonant absorption spectrum, we first apply an off-resonant laser pulse to ensure that the vacancy center is in the desired negative-charge state. Then we

perform a wavelength scan with the resonant laser and infer the excitation efficiency via phonon-sideband detection. Throughout all the measurement procedure, radio-frequency waves are applied continuously.

V. THEORY

Although we are interested in the negatively charged silicon-vacancy defect in 4H-SiC, it is beneficial to start the description of the structure with its counterpart in the cubic (3C) polytype. In this case, the defect has T_d point symmetry and its dangling bonds form an a_1 one-electron orbital and a t_2 one-electron orbital. In the negatively charged state, five electrons occupy these states, two on the lower-lying a_1 orbital and three on the t_2 orbital with parallel spins, leading to a quartet spin ground state. The first quartet excited state can be constructed by promoting an electron from the a_1 orbital to the t_2 orbital in the spin minority channel. This excited state is Jahn-Teller unstable, its T orbital symmetry will be broken by t_2 symmetric phonon modes ($T \times t_2$ problem) [27]. The hexagonal 4H polytype produces a hexagonal crystal field that statically breaks the tetrahedral symmetry. However, the key properties of the defect can be still derived from that high symmetry in the cubic crystal. This crystal field is axially symmetric in 4H-SiC (called the “ c axis”), lowering the T_d symmetry to its subgroup C_{3v} . In C_{3v} symmetry, t_2 splits to an a_1 orbital and an e orbital. Furthermore, we call the lower-lying a_1 orbital “ u ” and the higher one “ v .” Analogously, the ground-state configuration will result in a quartet 4A_2 . A lower excited state can be constructed by promoting an electron from the u orbital to either the v orbital (4A_2) or the e orbital (4E). The structure of the defect and its electron configurations are depicted in Fig. 1. The fine structure of the silicon-vacancy center was determined by Soykal *et al.* [28]. The orbital singlets are affected only by the spin-spin interaction, resulting in a splitting of the $\pm\frac{1}{2}$ and $\pm\frac{3}{2}$ Kramers doublets by $2D$ (dipolar electron spin-spin interaction). In 4E , axial spin-orbit coupling splits 8 times degeneracy (counting both the orbital and spin degeneracies) to four Kramers doublet levels with equal energy spacing of 2Δ . These are also affected by the spin-spin interaction analogously to the orbital singlets. The origin of vibronic coupling in this system can still be described by the $T \times t_2$ Jahn-Teller problem but in the presence of the perturbing C_{3v} crystal field. The potential-energy surfaces of the t_2 orbitals are formulated with pseudospin of three dimensions. Therefore, the vibronic interaction can be expressed on this basis as a 3×3 matrix:

$$\mathbf{W} = \begin{pmatrix} 0 & -F_T Q_\zeta & -F_T Q_\eta \\ -F_T Q_\zeta & 0 & -F_T Q_\xi \\ -F_T Q_\eta & -F_T Q_\xi & 0 \end{pmatrix}, \quad (1)$$

FIG. 1. Geometric and electronic structures of the negatively charged silicon-vacancy (V_{Si}) defect in 4H-SiC. (a) Atomic model of the defect at the h site showing C_{3v} symmetry. (b) Electronic structure of the spin-polarized 4A_2 ground state and the one-particle excitation schemes corresponding to the 4A_2 and 4E excited states. (c) Fine structure of the excited states regarding spin-orbit (SO) and dipolar spin-spin (SS) interactions (see Ref. [28]). CB, conduction band; VB, valence band.

where the orbital degrees of freedom ($t_2^{(\xi)}$, $t_2^{(\eta)}$, $t_2^{(\zeta)}$) are depicted by the rows and columns of the 3×3 matrix and the vibrational degrees of freedom are expressed by the Q_i configuration coordinates. The F_T linear vibronic coupling parameter connects the three T vibrational normal modes with the three t_2 orbitals depicted by the matrix. The linear vibronic coupling can be expressed with the Jahn-Teller energy as follows [see Eq. (3.48) in Ref. [27]]:

$$F_T = \sqrt{\frac{3}{2}} \hbar \omega E_{JT}. \quad (2)$$

The C_{3v} crystal field is introduced similarly to describe silicon vacancies in 4H-SiC. Thus, the adiabatic potential-energy surface (APES) on the t_2 basis,

$$\varepsilon(Q) = \frac{1}{2} \hbar \omega (Q_\xi^2 + Q_\eta^2 + Q_\zeta^2) \mathbf{I} + \mathbf{W} - \frac{\delta}{3} \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}, \quad (3)$$

consists of the phonon energy associated to the harmonic potential of the electronic APES ($\mathbf{I}$ is the identity matrix), the vibronic interaction, and the crystal-field splitting (δ). The associated Hamiltonian describes three coupled

three-dimensional harmonic oscillators:

$$\hat{H} = \hbar\omega \left(\hat{a}_\xi^\dagger \hat{a}_\xi + \hat{a}_\eta^\dagger \hat{a}_\eta + \hat{a}_\zeta^\dagger \hat{a}_\zeta + \frac{3}{2} \right) \hat{I} - F \left(\hat{T}_\xi \hat{Q}_\xi + \hat{T}_\eta \hat{Q}_\eta + \hat{T}_\zeta \hat{Q}_\zeta \right) - \frac{\delta}{3} \left(\hat{T}_\xi + \hat{T}_\eta + \hat{T}_\zeta \right), \quad (4)$$

where $\hat{a}_i^\dagger$ is the oscillator- i mode-creation operator, $\hat{Q}_i = \frac{1}{\sqrt{2}} (\hat{a}_i^\dagger + \hat{a}_i)$ are the coordinate operators, and the pseudospin of t_2 orbitals is represented by the orbital operators

$$\hat{I} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \hat{T}_\xi = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad (5)$$

$$\hat{T}_\eta = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \quad \hat{T}_\zeta = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

Projections of the electronic contributions in the vibronic states to the corresponding a_1 and e basis states of C_{3v} symmetry are constructed with use of the symmetrized combinations of the t_2 orbitals.

The thermal shift and broadening of the ZPL can be attributed mainly to the vibronic interaction of quasidegenerate orbitals, which are split by spin-orbit or crystal-field interaction, with acoustic phonons. This can be modeled by time-independent and time-dependent perturbation theory, resulting in a perturbed energy spectrum (shift) and transition rates (linewidth), respectively.

VI. RESULTS AND DISCUSSION

A. Polaronic spectrum in the excited state of V1 and V2 centers

We calculate the excited-state relaxed structures using Δ SCF method; therefore, the optical excitation is straightforwardly described by promotion of an electron to an unoccupied Kohn-Sham level. The calculated ZPL energies of the ${}^4A_2 \rightarrow {}^4A_2$ optical transition for V1 and V2 centers are 1.450 and 1.385 eV, respectively, and are in good agreement with experimental values. However, we find the second electronic excitation (${}^4A_2 \rightarrow {}^4E$) at much higher energies, 1.792 and 1.953 eV, respectively. The pure electronic excitation cannot account for the observed V1' state in the PL spectrum. We conclude that the observed V1' state should belong to a polaronic excited state with a mixed electronic character of 4A_2 and 4E . In the following, we explore the polaronic spectrum and the vibronic mixing in these quantum-bit defects to predict their magneto-optical properties as a function of temperature and strain.

We calculate the parameters in Eq. (3) with HSE06 DFT methods using a model of the silicon-vacancy center in

TABLE I. Jahn-Teller parameters of V1 and V2 centers obtained from DFT calculations.

Center	E_{JT} (meV)	$\hbar\omega$ (meV)	δ (meV)
V1	255.4	102.5	7
V2	396.5	127.5	29

quasi- T_d symmetry. As the Jahn-Teller effect originates from the occupational instability of degenerate orbitals, we can relax the system to the high-symmetry configuration by “smearing” the electronic occupation of the a_1 and e Kohn-Sham levels corresponding to the t_2 level. The smearing eliminates the origin of symmetry breaking, and thus orbital and geometric relaxation leads to the high-symmetry configuration. This is done by restricting equal occupation of the v and e orbitals to $\frac{1}{3}$ in the spin minority channel. Full self-consistent solution and structural relaxation of this constraint occupation of orbitals results in the spin quartet excited state with quasi- T_d geometry and wave functions. The remaining Kohn-Sham-level splitting of the v and e orbitals in this quasi- T_d configuration is attributed to the δ crystal-field splitting. Jahn-Teller instability of this excited state results in a symmetry breaking of quasi- T_d , which leads to the two C_{3v} branches that correspond to the 4A_2 and 4E excited-state APESs.

The Jahn-Teller parameters for V1 and V2 centers are calculated from the APES corresponding to quasi- $T_d \rightarrow C_{3v}$ distortion (see Table I). The calculated total energy difference of the high-symmetry quasi- T_d configuration and the low-symmetry C_{3v} configuration equals the E_{JT} parameter. From the high-symmetry and low-symmetry geometries, we calculate the normal coordinate distance of the relaxation in dimensionless units. From this result, we evaluate ω using the harmonic approximation of the APES. F_T is obtained from Eq. (2).

We calculate the polaronic spectrum with the following wave-function ansatz:

$$|\tilde{\Psi}\rangle = \sum_{n,m,k} (c_{nmk}^{(\xi)} |t_2^{(\xi)}\rangle + c_{nmk}^{(\eta)} |t_2^{(\eta)}\rangle + c_{nmk}^{(\zeta)} |t_2^{(\zeta)}\rangle) |n, m, k\rangle, \quad (6)$$

where we limit our phonon or vibrational expansion to eighth order: $(n + m + k \leq 8)$. Thus, in other words, we limit the $a_\xi^\dagger$, $a_\eta^\dagger$, and $a_\zeta^\dagger$ operators acting on the usual harmonic oscillator basis: $a_n^+ |n, m, k\rangle = \sqrt{n+1} |n+1, m, k\rangle$, $a_m |n, m, k\rangle = \sqrt{m-1} |n, m-1, k\rangle$. However, the symmetry of the polaronic system is reduced from T_d , and thus we project out the A_1 and E electronic characters of the polaronic states to C_{3v} point symmetry (see Table II), which is realized as our transforming the coordinate system of Eqs. (1), (3), and (5) toward the $[111]$ direction of cubic T_d symmetry. The $[111]$ direction corresponds the c axis of

TABLE II. Polaronic spectrum of V1 and V2 centers and the contribution of the electronic states belonging to the corresponding irreducible representation of the C_{3v} point group. We define the $|A_1\rangle\langle A_1|$, $|E_x\rangle\langle E_x|$, and $|E_y\rangle\langle E_y|$ projectors as defined by Eq. (7) for the A_1 , E_x , and E_y contributions.

Relative energy (meV)	A_1 contribution	E_x contribution	E_y contribution
V1 center			
0.000	0.84	0.08	0.08
4.829	0.12	0.67	0.21
4.829	0.12	0.21	0.67
20.081	0.26	0.37	0.37
66.607	0.53	0.12	0.35
66.607	0.53	0.35	0.12
V2 center			
0.000	0.94	0.03	0.03
22.070	0.14	0.21	0.65
22.070	0.14	0.65	0.21
32.824	0.18	0.41	0.41
89.576	0.69	0.08	0.23
89.576	0.69	0.23	0.08

4H-SiC and the a and b axes depicted by the plane perpendicular to it spanned by vectors $[1\bar{1}2]$ and $[1\bar{1}0]$ as depicted by the following equations:

$$\begin{aligned}
 |A_1\rangle &= (|t_2^{(\xi)}\rangle + |t_2^{(\eta)}\rangle + |t_2^{(\zeta)}\rangle)/\sqrt{3}, \\
 |E_x\rangle &= (-|t_2^{(\xi)}\rangle - |t_2^{(\eta)}\rangle + 2|t_2^{(\zeta)}\rangle)/\sqrt{6}, \\
 |E_y\rangle &= (|t_2^{(\xi)}\rangle - |t_2^{(\eta)}\rangle)/\sqrt{2}.
 \end{aligned} \tag{7}$$

On the basis of these results, we attribute the V1' ZPL line to the transition that connects the first polaronic excited state of predominantly E electronic character to the electronic ground state. This way, the measured energy difference of V1 and V1' agrees well with the first polaronic excitation energy $\Delta_p \sim 5$ meV. We can similarly predict its V2' counterpart to be $\Delta_p = 22$ meV higher in energy than V2. The lack of the second sharp emission in the V2 center in the experiments may be explained by the relatively large energy spacing between the V2 and V2' states because a V2' state could be occupied at around room temperature in the PL measurements that overlaps with the sideband of the acoustic phonon modes.

From the polaronic mixing of electronic states obtained, we determine the orientation of the optical polarization associated with V1 and V1' transitions. From the optical selection rules, optical transition between pure electronic states $A_2 \leftrightarrow A_2$ and $A_2 \leftrightarrow E$ is allowed by $p_{\parallel}$ and $p_{\perp}$ polarization, respectively. Parallel coincides with the c axis of the crystal. As V1 and V1' transitions are the polaronic mixture of the above, the observed polarization shows an

inclination from the parallel direction with an angle of

$$\varphi = \arctan\left(\frac{c_A^2 \mu_A^2}{c_E^2 \mu_E^2}\right), \tag{8}$$

where c_A^2 and c_E^2 are the respective A_1 and $E_x + E_y$ contributions in Table II for the corresponding polaronic state. Relative transition dipole strength $\mu_A^2/\mu_E^2 = 0.57$ is obtained with the same method as discussed in Ref. [29]. The resulting angles of optical polarizations from Eq. (8) are $\varphi = 18^\circ$ and $\varphi = 86^\circ$ for V1 and V1' transitions, respectively. These are comparable to the experimental findings of approximately 30° and approximately 90° in Ref. [30].

B. Zero-field splitting in the polaronic excited state

We use HSE06 ZFS parameters of the 4A_2 and 4E electronic configurations to calculate the ZFS in polaronic states as a contribution-weighted average of the electronic characters. With the calculated ZFS parameters of $2D_{4A_2} = 1664$ MHz and $2D_{4E} = -1216$ MHz, the first polaronic state has $2D = 1211$ MHz ZFS for the V1 center. Similarly, we obtain the polaronic-excited-state ZFS of $2D = 1400$ MHz from $2D_{4A_2} = 1569$ MHz and $2D_{4E} = -1172$ MHz for the V2 center. Here we ignore any spin-orbit interaction in the 4E excited state. The validity of this approximation is detailed in Sec. IV E. We calculate the temperature dependence of the ZFS for V1 and V2 centers using the Boltzmann-factor-weighted-average ZFS from the polaronic states at the sampling temperatures. We predict a rapid decrease for the V1 center that goes to negative values for high temperature. The V2 center shows a slower transient and decrease; however, Anisimov *et al.* [13] measured an even-more-moderate slope that looks almost linear (see Fig. 2). We measure the ZFS in cryogenic temperature range using PL. The trends here follow the DFT calculations closely. The calculated values are shifted for direct comparison with the experimental data (shifting values in the caption of Fig. 2). Our DFT-calculated D parameters are generally overestimated compared with the experimental ones as a consequence of spin contamination. The polaronic solution carries this systematic error as well. Furthermore, our vibronic solution relies on an effective single-phonon model that cannot incorporate the features of the phonon sideband with acoustic phonon modes. This can also result in a steeper convergence to a low ZFS in the high-temperature limit. At higher temperatures, the more-pronounced mixing of electronic characters should lead to an averaging to T_d symmetry, where the ZFS should vanish. The experimental low-temperature and high-temperature limits suggest that the intrinsic ZFS should be around 1200 MHz in the 4A_2 excited electronic state and around -450 MHz in the 4E excited electronic state.

FIG. 2. Temperature dependence of the excited-state zero-field splitting in V1 and V2 centers (a) at cryogenic temperatures and (b) in a wider temperature range. Solid curves are calculated from the Boltzmann statistics of the polaronic states with specific zero-field-splitting values from the vibronic mixing. The calculated ZFS curves are shifted by 211 MHz (V1 DFT) and 378 MHz (V2 DFT) for comparison with the trends of our observed PL data in (a) and previous experimental data in (b) from Ref. [13] derived from optically-detected-magnetic-resonance (ODMR; solid circles) and level-anticrossing (LAC; hollow circles) measurements.

C. Temperature-dependent PL linewidth

Besides the temperature dependence of the fine structure, our polaronic solution can model the temperature dependence of the PL linewidth as well. We expect a broadening due to the mixing of polaronic states mediated by phonons. At cryogenic temperatures, acoustic phonons dominate due to their small energy, resulting in a significant occupation number. At higher temperatures, the rapidly increasing linewidth makes the transitions between $m_S = \pm 1/2$ and $m_S = \pm 3/2$ indistinguishable. As the polaronic gap is quite large compared with spin-orbit splitting, we expect that only single-phonon-mediated processes give a contribution with resonant phonon frequency to the polaronic gap. This can be formulated similarly to a resonance process in time-dependent perturbation theory, where the total transition rate would be temperature

FIG. 3. Temperature-dependent linewidth of the observed PL signal fit by a single-phonon-absorption model [see Eq. (9)] to the averaged $m_S = \pm 1/2$ (hollow points) and $m_S = \pm 3/2$ (solid points) transitions of V1 and V2 centers.

dependent owing to the Bose-Einstein statistics of the acoustic phonons [31]. This is a temperature-activated process with the specific polaronic gaps (Δ_p) as activation energies for V1 and V2 centers. The linewidth scales with Δ_p^3 owing to the product of linear and quadratic frequency scaling of the squared vibronic interaction strength and phonon density of states, respectively. We ignore the temperature dependence of Δ_p that would result in a higher-order correction. As Δ_p values are much larger than the usual spin-orbit splitting of degenerate orbitals, we expect to see only the transient start of the linear dependence at cryogenic temperatures ($T < 30$ K). Owing to the difference in the vibronic gaps, we expect the broadening of PL lines to start at lower temperatures for the V1 center than for the V2 center. We perform temperature-dependent PL measurements for both centers (see Fig. 3) and fit the above model for the linewidth as

$$\Gamma(T) = \frac{A\Delta_p^3}{\exp \frac{\Delta_p}{k_B T} - 1} + \Gamma_r + \Gamma_1, \quad (9)$$

where the first fitting parameter, A , incorporates the average acoustic phonon density and the coupling strength. $1/\Gamma_r = (2\pi)6$ ns is the measured PL transition rate. The second fitting parameter, Γ_1 , comprises all additional temperature-independent linewidth-broadening processes, such as laser-power broadening and spectral diffusion. Here we assume that spectral diffusion can be described by a temperature activated process with activation energy much greater than Δ_p ; thus, it has negligible temperature dependence at low temperatures. The parameters obtained after this fitting procedure are summarized in Table III.

D. Coherence of the optical emission

After consideration of the dephasing of the ZPL line caused by the acoustic phonons, we turn our attention to

TABLE III. Fit parameters in the model of Eq. (9).

Center	A (GHz/meV ³)	Γ_1 (GHz)
V1	0.37 ± 0.03	0.065 ± 0.004
V2	0.26 ± 0.02	0.082 ± 0.003

the overall coherence of the emission. This is characterized by the ratio of ZPL emission to the total emission, called the “Debye-Waller factor.” To study this, we measure the PL signal of the silicon-vacancy centers and calculate the phonon sideband using Huang-Rhys theory [32]. The high-precision Δ SCF geometry optimization enables a good approximation for the phonon-assisted transitions. In this method, we rely on the simplified Frank-Condon principle [33,34], where we use the calculated ground-state phonon spectra and normal modes. The calculation shows excellent agreement with the experimental signal (see Fig. 4). The calculated Huang-Rhys factors (S) are relatively large at 0 K, and consequently the Debye-Waller factor is about 6% for both centers. The experimental Debye-Waller factors are about 8% and 9% for V1 and V2

FIG. 4. Experimental and calculated photoluminescence sideband of (a) V1 and (b) V2 centers. Calculated Huang-Rhys factors (S) are shown. All experimental data are corrected for spectrometer efficiency.

centers, respectively. Our measured Debye-Waller factor deviates from the previously reported value [4]. We associate the discrepancy with the limited spectral range of the spectrometer used in the previous studies.

E. The effect of spin-orbit coupling on the fine structure of the excited state

Next we consider the effect of spin-orbit coupling in the 4E excited state for two reasons. Firstly, we need to estimate its contribution to the zero-field splitting in the excited polaronic state. Secondly, the intrinsic spin-orbit-coupling strength is an important factor for the rates of intersystem crossing toward the doublet states. We calculate an intrinsic spin-orbit-coupling strength of $\lambda_{\parallel} = 6\Delta = 0.29 \pm 0.04$ meV for the V1 center and $\lambda_{\parallel} = 0.41 \pm 0.04$ meV for the V2 center by calculating the spin-orbit splitting of e Kohn-Sham orbitals in the quasi- T_d excited state. These values with the corresponding standard deviation are obtained by our fitting an exponential convergence for the increasing size of the supercell (see Fig. 5). The strength of the spin-orbit coupling obtained is an order of magnitude smaller than the crystal field, which implies that the perpendicular component of the spin-orbit coupling has a very weak contribution in second-order perturbation theory. Furthermore, the parallel component can be considered as a small, independent perturbation of the electron-phonon system. By adding $H_{SO} = \lambda_{\parallel} \mathbf{L} \cdot \mathbf{S}$ to the electron-phonon Hamiltonian in Eq. (3), we obtain contributions of 20–80 MHz and -5 to -20 MHz from spin-orbit coupling to the D parameter for the V1 center in the first polaronic branch (4A_2) and the second polaronic branch (4E), respectively. These values are minor corrections, as they are at least an order of magnitude smaller than the original ZFS of around 1 GHz. The second polaronic excited state has spin-orbit parameter $\Delta = 3.3 \pm 1$ GHz, which is of the expected order of magnitude [35]. In conclusion, the effect of spin-orbit coupling can

FIG. 5. Size scaling of parallel spin-orbit coupling in the quasi- T_d excited-state configuration of V1 and V2 centers.

be treated as a perturbation compared with the vibronic coupling, resulting in minor corrections in the polaronic spectrum and in the dipolar electron spin-spin zero-field splitting.

F. Crystal strain effect on the ZPL position

Knowledge of the effects of crystal strain on the optical properties of the quantum defect is also an important factor in many applications; however, these are yet to be measured for the *h*-site and *k*-site silicon-vacancy defects in 4*H*-SiC. To determine these, we calculate the strain dependence of the ZPL position for normal strain components. We specify the strain matrix in the cubic reference frame, where *z* and *x* coincide with the [0001] and [1 $\bar{1}$ 00] directions in the hexagonal reference frame, respectively. This choice makes the *x*-*z* plane a vertical mirror plane. We deform the 4*H*-SiC supercell according to a single strain-matrix element and allow the defect to relax under the effect of strain. We calculate the ZPL energy for a set of seven equidistant points in the range from -0.003 and 0.003 strain, and fit the slope (*a*) to a linear function. The resulting ZPL-strain coupling strengths of V1 and V2 centers are listed in Table IV.

These strain dependencies can be demonstrated in a simplified picture, where the changes in the ground-state Kohn-Sham defect levels are followed. The analogy to the ZPL is the energy difference of the *u* and *v* defect levels in this approximation [see Fig. 1(b)]. Compressive strain increases the charge density of the defect orbitals, leading to stronger repulsion between them, whereas the opposite can be stated for tensile strain. We find this closing tendency of the *u* and *v* energy gap in the calculations (see Fig. 6), which can be interpreted as a negative slope in the ZPL. Furthermore, the *v* orbital is more localized on the axial carbon first neighbor of the vacancy than on the basal ones [29], resulting in a larger response for axial strain (*a_{zz}*) compared with basal components (*a_{xx}* and *a_{yy}*).

With piezoelectric actuators, a transverse tensile strain of up to 7.5×10^{-5} was demonstrated in 4*H*-SiC [36]. This could result in a shift of around -0.1 meV in the ZPL. According to our simulations, a larger shift in the ZPL can be obtained by application of a tensile strain parallel to the *c* axis. Pneumatic press on the sample can readily cause a large compressive strain on the order of 10^{-3} that could lead to a shift of several millielectronvolts in the ZPL transitions. This strong coupling to strain can be harnessed in quantum-communication applications, where

TABLE IV. Calculated ZPL-strain coupling parameters for the V1 and V2 centers in 4*H*-SiC.

Center	<i>a_{xx}</i> (eV/strain)	<i>a_{yy}</i> (eV/strain)	<i>a_{zz}</i> (eV/strain)
V1	-1.06 ± 0.08	-1.41 ± 0.03	-7.40 ± 0.02
V2	-1.97 ± 0.09	-1.89 ± 0.07	-6.25 ± 0.05

FIG. 6. Strain dependence of the Kohn-Sham levels in the ground state of the V1 center. *u*, *v*, and *e* are the defect levels depicted in Fig. 1(b). VBM, valence-band maximum.

identical emitters are needed for efficient coupling of distant qubits with photons. An efficient control of the ZPL position compensating for local differences (e.g., temperature) could be achieved by application of a specific strain using piezoelectric actuators.

VII. CONCLUSION

We investigate the negatively charged silicon-vacancy defects in 4*H*-SiC at the hexagonal and cubic sites, called “V1 and V2 PL centers.” We take electron-phonon interaction into account to describe their magneto-optical properties and their coupling to external perturbations. We represent this interaction on the basis of the quasitetrahedral symmetry of the defect that is lowered by the crystal field of the host. We accurately reproduce the V1’ level as a vibronic excited state and predict the V2’ counterpart. We predict the temperature dependence of the optical linewidth and zero-field splitting, which show different features for the two defects. We also determine the normal strain dependence of the ZPL position on the order of magnitude of electronvolts per strain. Finally, we obtain intrinsic spin-orbit-coupling parameters of about 0.3 and 0.4 meV for V1 and V2 centers, respectively; these do not contribute to the temperature dependence but are important in understanding the intersystem-crossing processes.

The physics of the vibronic coupling in the excited state is closely related to quantum applications, notably those requiring emission of highly indistinguishable photons. This comprises distribution of remote entanglement via photonic interference in a quantum-repeater network [37] and generation of photonic cluster states for measurement-based quantum computation [38,39]. The discussed interaction process with phonons in the excited state is directly related to the rate of pure dephasing of a single-photon state, which affects the photon indistinguishability [40]. Further, strain tuning of the ZPL emission, as discussed

in this work, can provide an efficient means to match the photon emission wavelengths of multiple defects or to tune emitters into resonances of optical cavities to increase photon emission rates.

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