Isolated electron spins in silicon carbide with millisecond coherence times

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1 Supplementary methods.

Our experimental setup is a home-built, near-infrared confocal microscope, and a simplified diagram of it is presented in Fig. S1. A 330 mW 975 nm continuous wave diode laser (ThorLabs, PL980P330J) used for exciting the divacancy defects is coupled through a single mode fiber into free space using an aspheric lens. The beam is attenuated and focused using a neutral density filter wheel and focused through a lens into an acousto-optic modulator to obtain a rise time of about 10 – 20 ns. The diffracted beam is focused into a Corning SMF-28e+ single mode fiber attached to three paddles that allow us to adjust the polarization using the birefringence of the fiber under strain (ThorLabs, FPC561). The combination of the acousto-optic modulator and re-focusing the beam into a single mode fiber provides a DC on/off contrast of about 47 dB. The beam is spectrally filtered using a 975 nm bandpass filter (Edmund Optics, 87-798), expanded and collimated using a lens pair, and linearly polarized using a Glan-Laser polarizer. The excitation is incident on an angled 1064 nm dichroic beamsplitter (Semrock, LPD01-1064RS). This beamsplitter nominally reflects 1064 nm light at a 45° angle of incidence and transmits longer wavelengths, so the beamsplitter is rotated to blueshift the turn-on wavelength and maximize the reflection of the excitation light. The beam is passed through a half-wave plate affixed to a motorized rotation mount (Standa, 8MR151) that allows fine angular control. A fast steering mirror (Newport, FSM-300) steers the beam before it is passed through an imaging lens pair. A periscope mirror pair affixed to three perpendicular stages (Newport, VP25XL) allows three dimensional movement. The beam overfills a 100x, 0.85 numerical aperture, 1.2 mm working distance, near infrared objective, also mounted to the periscope assembly, that has up to a 0.7 mm coverslip correction (Olympus, LCPLN100XIR). The beam finally passes through the custom 0.65 mm thick, anti-reflection coated, infrared fused silica window (Rocky Mountain Instruments) of our helium flow cryostat (Janis, ST-500) and is incident on the sample. The photoluminescence (PL) is collected back through the objective and transmitted through the dichroic beamsplitter. Another dichroic beamsplitter (Semrock, LPD01-1064RS) is used as a tunable filter to eliminate PL between about 1.0 µm and 1.1 µm, which was found to materially reduce the unidentified broad background PL in that region. A 1.0 µm long pass filter (ThorLabs, FELH1000) is used to eliminate any scattered light from the excitation laser. The light is focused into an anti-reflection coated SMF-28e+ single mode fiber. For Hanbury-Brown and Twiss measurements, the beam can also be split by a near infrared coated, non-polarizing beamsplitter, and focused into two different SMF-28e+ fibers. Each fiber is connected to a detector port on a commercial NbTiN superconducting nanowire single photon detector system (SingleQuantum, EOS). These detectors have approximately 28% quantum efficiency about 100 dark counts per second at the bias currents we use for each detector channel (17 µA and 24 µA). The detectors reside inside a closed cycle cryogenic system, which operates at about 3.1 K. The detectors have a manufacturer-specified timing jitter of about 50 ps. Pulses from the first detector channel are split using a power splitter (MiniCircuits). One path is connected directly to our time correlated photon counting module (PicoHarp, PH300) and the other is passed into a pulse converter (Horiba, TB-01) to convert the short detector pulses into longer TTL pulses that are passed through a switch (MiniCircuits, ZASWA-2-50DR+) and counted by a data acquisition.
Figure S1: Diagram of experimental apparatus.
card (National Instruments, X Series). The second detector channel is connected to the other port of the time correlated photon counting module and was only used in this work for anti-bunching measurements. For measurements of PL in the confocal measurement geometry, the second single mode fiber is instead connected to a 62.5 µm core multimode fiber whose output is coupled into an Acton SP-2300i spectrometer. The 0.3 m spectrometer uses a 1.2 µm blaze, 150 g/mm grating to diffract the light onto a Princeton Instruments OMA V InGaAs linear photodiode array. The 1024-pixel photodiode array is cooled to approximately −95°C using liquid nitrogen. The system is calibrated across multiple wavelengths using a Hg(Ar) lamp source, and has a wavelength accuracy of about σ = 0.2 nm for the measurements on a single defect.

Within the cryostat, samples are mounted directly on top of a coplanar waveguide (CPW) designed for 50 Ω impedance using rubber cement (Elmer’s, No-Wrinkle Rubber Cement). The CPW is 254 µm thick, fabricated on a Rogers RT/duroid 6002 substrate, and affixed to the coldfinger using solder on the backplane. The CPW is shorted at the end, and fed by a coaxial line connected to a hermetically sealed feedthrough. The RF signals are generated by a microwave signal generator (National Instruments, PXIe-5652) near 1.3 GHz. They are gated into rectangular pulses using a digital delay generator (SRS, DG645) and a switch (MiniCircuits, ZASWA-2-50DR+) and passed through a 30 W broadband amplifier (MiniCircuits, ZHL-30W-252) before entering the cryostat. A resistive heater in the cryostat and a PID controller maintains the cryostat at T = 20 K with a stability of better than 0.01 K. A custom goniometer with permanent magnets allows the application of a magnetic field along adjustable polar and azimuthal angles with precise radial positioning using a motorized linear stage (Newport, IMS-100).
2 Measurements of photoluminescence.

A bulk PL spectrum from the sample irradiated at the highest fluence (1 × 10^{15}/cm^2) is shown in Fig. S2. These data were collected using a 14 mm lens instead of an objective, and by focusing the emitted fluorescence into a multimode fiber that is coupled to an InGaAs detector-array spectrometer. Three of the four zero phonon lines associated with neutral divacancies are labeled, but the fourth line from the (hk) defect, which should appear near 1.11 μm, was not observed. Optically detected magnetic resonance measurements in the confocal geometry using the high-NA objective also never showed a luminescent point source having a resonance associated with the (hk) divacancy. The broad PL after the turn-on of our filter, near 1.0 μm, but before the (kh) zero phonon line is not understood, but believed to be a primary component of the background PL observed in our measurements.

![Bulk photoluminescence spectrum](image)

Figure S2: Bulk photoluminescence spectrum. PL spectrum collected at \(T = 20\,\text{K}\) using a non-confocal geometry from the sample irradiated at the highest fluence of 1 × 10^{15}/cm^2. Zero phonon lines associated with the (hh), (kk), and (kh) defects are labeled. The line labeled “Raman” is the Raman-shifted excitation laser and not a zero phonon line.

To investigate the nature of the background PL as well as to measure the spectrum of a single defect, the same beamsplitter employed for the antibunching measurements is again used to split the PL into separate single mode fibers while the confocal excitation and collection spot is centered on the single (kk) defect presented in the main text. The second fiber is coupled into an InGaAs spectrometer array. The same feedback loop used to maintain the alignment of the apparatus
on a single defect for the other measurements in this work is run periodically between 90 s long spectrometer acquisitions. Spectra are repeatedly acquired while on the single (kk) defect with the excitation laser on, while on the single (kk) defect with the excitation laser off, and while displaced to a dark region containing just background PL approximately 2 μm away with the laser again on. These spectra are collected in randomized order to average away any slow fluctuations, and the integrated spectrum collected with the laser off is subtracted from the other two spectra to remove the detector dark counts, yielding the data plotted in Fig. S3(a).

The background-only spectrum has a sharp line near 1057 nm that we have confirmed in the past is the Raman-shifted excitation laser, and accounts for about 12% of the total background signal. The broad background above the turn-on edge of the dichroic at 1100 nm (including the small peak near 1079 nm that is a non-ideality of the dichroic filter) has an origin that is less clear. No obvious peaks that might be seen in the phonon sideband of a defect are obvious, but the signal-to-noise ratio is too low to draw a reliable conclusion.

Subtracting the PL of the background from the PL measured on the single defect gives the data plotted in Fig. S3(b), which shows no Raman peak and no (kh) zero phonon line as expected. These data are corrected using a calibrated white light source to within about 10%. We can calculate a rough approximation of the Debye-Waller factor of (5.3 ± 1.1)% by computing the fraction of total PL in the zero phonon line. We also measure time resolved PL from the same single (kk) divacancy acquired by counting the pulses received by the data acquisition card in 30 Hz intervals and scaling these counts by the interval to recover the countrate. The time trace (decimated by a factor of five) along with a histogram of the full dataset acquired over a 200 s period are shown in Fig. S4. The red curve over the histogram is the maximum likelihood estimate of the density assuming the data follow a Poisson distribution, showing that the defect is photostable. As an additional note, we have never observed any evidence of photoinstability during any measurements of the samples in this work.
Figure S3: **Confocal PL spectra.** a, Spectra collected on and off a single $kk$ divacancy. The spectrum collected on the defect is offset by 2000 units for clarity. b, Subtracted spectra that show the spectrum of a single $kk$ divacancy. The zero-phonon line of the $kk$ divacancy PL at 1131 nm is limited by the resolution of our spectrometer.
Figure S4: **Measurement of divacancy photostability.** A time trace of the PL intensity measured by the single photon detector while focused on the single (kk) divacancy. The histogram bins the counts and the maximum likelihood estimate assuming a Poisson distribution is normalized to the histogram height and plotted over it. The single rate parameter Poisson distribution agrees well with the data, further indicating the defect is photostable.
3 Scaling of Rabi oscillations with applied power.

Figure S5: Rabi frequency scaling with applied microwave power. The data are the 95% intervals from fits to separate Rabi oscillation measurements incorporating a 0.26 dB systematic uncertainty in the variable attenuator we use. The red line is a fit to the form $a\sqrt{P}$, where $a$ is a free parameter and $P$ is the applied microwave power in arbitrary units. The nominal powers range from 31.0 dBm to 44.0 dBm at the input of the cryostat. This relationship should be linear and the data agree to within the error.
4 Additional data on a single (kk) divacancy spin coupled to a nearby nuclear spin.

Figure S6: Coherent control of a hyperfine-coupled single (kk) divacancy spin. a, Photon antibunching data with $g^2 < 0$, indicating the PL originates from a single defect. b, Continuous wave optically detected magnetic resonance near $B = 52 \, \text{G}$ showing a $13.4 \, \text{MHz}$ splitting due to a nearby Si$^{29}$ nuclear spin. c, Rabi oscillations from the hyperfine-coupled spin. The oscillations are driven at low power to selectively drive only one of the hyperfine resonances.
5 Analysis of photon anti-bunching measurements.

Because of surface-related PL, we mostly measured defects that are approximately 20 µm into the sample. At these depths, the background signal was smaller, though still non-negligible at about 40%. The average count rate centered on a defect was measured, as well as the average of the count rate at four points (up, down, left, and right) each displaced approximately 1.2 µm away from the defect but within the same focal plane.

The ideal second order coherence function, \( g^2(t) \), is related to the raw counts (including background) from the experiment, \( N(t) \), by the relation,

\[
g^2(t) = \frac{N(t) / N_s - (1 - \rho^2)}{\rho^2},
\]

where \( N_n \) is a constant that normalizes the raw data to unity at long time delays, and \( \rho = S/(S+B) \), where \( S \) is the count intensity attributed only to the emitter (signal) and \( B \) is the background count intensity \( (S1) \). \( \rho \approx 0.45 \) was typical for the data presented in this work.

The expression for a two-level system, \( g^2(t) = 1 - Q \cdot \exp\left(-|t-t_0|/\tau\right) \) was found to have good agreement with our data \( (S2) \). Here, \( t_0 \) is the “zero delay” time and \( Q \) is the depth of the antibunching dip. A value of \( Q > 0.5 \) means \( g^2(t = t_0) < 0.5 \), which is indicative of a single emitter. The time constant, \( \tau \), is related to the optical lifetime of the defect, \( \tau_0 \), and the optical pumping rate, \( r \), by \( \tau = 1/(1/\tau_0 + r) \). A more detailed analysis can account for the existence of a third level, similar to the slowly relaxing singlet states in the diamond nitrogen vacancy center, but meaningful inference of those rate parameters requires a more detailed characterization of excitation powers and lifetimes outside the scope of this work.

For small values of \( \rho \) like in the present experiments, the background correction defined by Eq. S1 is very sensitive to the precise value of \( \rho \). For instance, \( \rho = 0.4 \) will “stretch” the antibunching dip by a factor of about 6.25, while \( \rho = 0.5 \) will only stretch the dip by about a factor of 4. Small changes, therefore, can produce a dip that goes below zero (non-physical) or is erroneously above 0.5 when measuring a single defect (a false negative). Moreover, low count rates and high background reduce the signal-to-noise of the measurement, requiring more rebinning of the raw data to make the dip obvious by eye, which distorts the depth of the antibunching dip upward.

The re-binned data taken on the isolated divacancies is what is displayed in all figures, but to eliminate the aforementioned issues, we applied a Bayesian approach using Poisson uncertainties on the raw data and normally distributed uncertainties on \( S \) and \( B \) to infer the parameters \( Q, \tau, t_0, \) and \( N_n \). Using this technique avoids introducing artifacts from rebinning, accurately propagates uncertainties in \( S \) and \( B \) (which are the components of \( \rho \)), and gives consistent point estimates and error bars of \( Q \) only in the physical range where \( g^2(t = t_0) \geq 0 \). The integrals in Bayesian models are often difficult to calculate analytically and so most practitioners calculate them via a simulation technique called Markov Chain Monte Carlo, which we use here to accomplish this as well \( (S3) \). The maximum \( \text{a posteriori} \) probability (MAP) estimate from the simulation was used to generate the fit curves plotted over the data for the three divacancies in the main text and the hyperfine-coupled divacancy in the Supplementary Information. The only prior pieces of
information incorporated into the model are the values and uncertainties for $S$ and $B$ measured periodically throughout the antibunching measurement, and that $Q$ is bounded between 0 and 1. The highest posterior density (HPD) credible intervals around the MAP value for $Q$ were $Q_{hh} = 0.91^{+0.09}_{-0.10}$, $Q_{kk,\text{hyperfine}} = 0.998^{+0.002}_{-0.021}$, $Q_{kk,\text{no hyperfine}} = 0.92^{+0.08}_{-0.21}$, and $Q_{kh} = 0.99^{+0.01}_{-0.14}$, at the 95% significance level, allowing us to claim with statistical rigor the detection of isolated defects ($S4$).

## 6 Electron spin echo envelope modulation (ESEEM)

The Hahn echo data in Fig. 3 are collected using standard two-pulse Hahn-echo sequence readout using optically detected magnetic resonance, namely “Initialize - $\pi/2 - t_{\text{free}}/2 - \pi - t_{\text{free}}/2$ - Readout”. For the single-spin Hahn echo measurement in Fig. 3b, the initialization and readout steps are a 1.8 µs laser pulse. We collect the first 220 ns of the photons emitted in the readout pulse. The arbitrary waveform generator used for timing our experiments jumps between sequences where the phase of the final pulse is positive and negative with the same pulse. The arbitrary waveform generator used for timing our experiments jumps between sequences.

For the ensemble Hahn-echo measurement in Fig. 3c, the initialization step is a 200 µs 975 nm laser pulse, and the readout step consists of a final $\pm \pi/2$-pulse to rotate the spin echo along measurement axis followed by a 50 µs laser pulse for readout. The PL intensity is measured with an InGaAs femtowatt photoreceiver, and a lockin amplifier demodulates the differential signal from the alternating phase of the final $\pi/2$-pulse. The plotted Hahn-echo coherence ($C$) in both the single-spin and ensemble Hahn-echo measurements is the differential PL intensity normalized such that $C = 1$ at $t = 0$.

The ESEEM data follow the general form,

$$C(t) = e^{-\left(\frac{t}{T_2}\right)^2} \prod_{j} \left(1 - K_j \sin^2 (\omega_j t)\right)^{N_j},$$

where the $\omega_j$ are the relevant ESEEM frequencies, the compressed exponential prefactor represents decoherence, and the $K_j$ and $N_j$ determine the ESEEM shape ($S5$). For the single-spin data in Fig. 3b, two ESEEM frequencies are used: $\omega_1$ and $\omega_2$ are set to be the Larmor precession frequencies of the $^{29}\text{Si}$ and $^{13}\text{C}$ nuclei respectively. The single-spin model fixes $N_1 = N_2 = 1$, and the decoherence term is neglected, since $T_2$ significantly exceeds the free precession times measured in the single-spin data. For the ensemble Hahn-echo data in Fig. 3c, three ESEEM frequencies are used in the fit: $\omega_1$ and $\omega_2$ are set to be the Larmor precession frequencies of the $^{29}\text{Si}$ and $^{13}\text{C}$ nuclei respectively, as before, and $\omega_3$ is left as a fitting parameter that can freely capture more complicated ESEEM dynamics.

This fit yielded $T_2 = (1.2 \pm 0.1)$ ms and $n = (2.0 \pm 0.3)$, as quoted in the main text. The interference term $\omega_3$ is fit to 58.6 kHz, slightly above the $^{29}\text{Si}$ nuclear precession frequency of 58 kHz. Although the origin of this term is not currently understood, it captures the beating effects seen in Fig. 3c (i.e. the ESEEM magnitude decaying more quickly than the overall coherence).
In addition to Fig. 3c, which presents ensemble Hahn-echo data extending to $t_{\text{free}}/2 = 1\text{ ms}$, we also show Hahn-echo data extending to $t_{\text{free}}/2 = 2\text{ ms}$ in Fig. S7. For these data, we did not attempt to fit the full ESEEM curve, but rather, we averaged the ESEEM oscillations and simply fit them to a compressed exponential of the form $e^{-\frac{t_{\text{free}}}{2T_2}}$. In this fit, we find that $T_2 = (1.25 \pm 0.05)\text{ ms}$, and $n = (2.0 \pm 0.2)$. 

Figure S7: Additional coherence data on the $(kk)$ divacancy ensemble.
References


