Evolution of the optically detected magnetic resonance spectra of divacancies in 4H-SiC from liquid helium to room temperature

Supplemental Material

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1. Experimental geometry

As mentioned in the experimental part of the main text, the excitation and the luminescence collection must be performed through the edge of nominal c-plane sample to be able to apply excitation and/or register photoluminescence with parallel to the c-axis polarization. Efficient coupling to the microwave (MW) field is needed to measure the ODMR spectra. In our study, the MW antenna is a copper wire with diameter 50 µm and it is placed on the c-face of the sample very close to the edge, as shown schematically in Fig. S1(a). Since the excited volume of the sample (i.e., the laser spot) must be close to the MW antenna, it is also close to the surface of the sample – the PL is excited in and collected from the edge of the sample but very close to the c-face surface. This stipulates the appearance of relatively strong PL5, PL6 and PL3a lines. These are not observed at all in the bulk (see the main text), which agrees with the previous suggestion that they are due to divacancies near stacking faults, because stacking faults are expected near the polished surfaces of the samples [1].

We notice that coupling of the MW antenna to the excited volume near the middle of the edge of the sample (the edge thickness is ~350 µm) requires positioning of the antenna near the middle of the edge along it [Fig. S1(b)]. Coupling for such configuration did not succeed, most probably because the cleaved edge of the sample is not sufficiently flat.

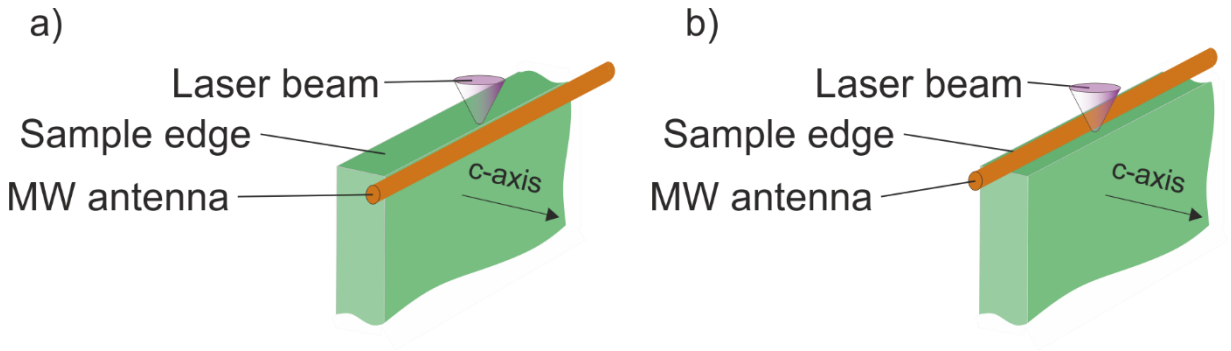

Fig. S1. (a) Schematic of the experimental geometry used throughout this work. The laser beam is very close (within 10 µm) from the surface (c-face) of the sample. (b) Experimental geometry which would cancel the contribution of PL5, PL6, and PL3a to the ODMR and PL spectra. Coupling to the MW field, however, has not been implemented in our experiments.

2. On the selection rules in excitation at elevated temperatures

In a previous publication [2], we show that the for the axial configurations of the divacancy (PL1, PL2, and PL6) of C_{3v} symmetry, the following selection rule for the polarization of the exciting

laser is valid: the axial configurations cannot be excited in photoluminescence if the laser polarization E_L is parallel to the c-axis, $E_L \| c$. In this work [2], evidence for this selection rule was presented mainly at liquid helium temperature because the ZPLs of the various configurations vanish at elevated temperatures. However, the peaks in the ODMR spectrum remain quite sharp at all investigated temperatures and may serve as an indicator of whether certain configuration is excited or not. Thus, the results of our study show that the selection rule quoted above remains valid, at least for the temperature interval investigated. This can be seen, for instance, by comparing the ODMR spectra in Figs. 1 and 3 of the main text. Further illustration is given by Fig. S2 comparing the ODMR spectra measured with $E_L \perp c$ and $E_L \| c$ at room temperature. It is apparent that the contribution in ODMR from PL1 and PL6 (axial configurations of the divacancy) vanish with $E_L \| c$ polarization, hence confirming the validity of the above-mentioned selection rule also at room temperature, as expected.

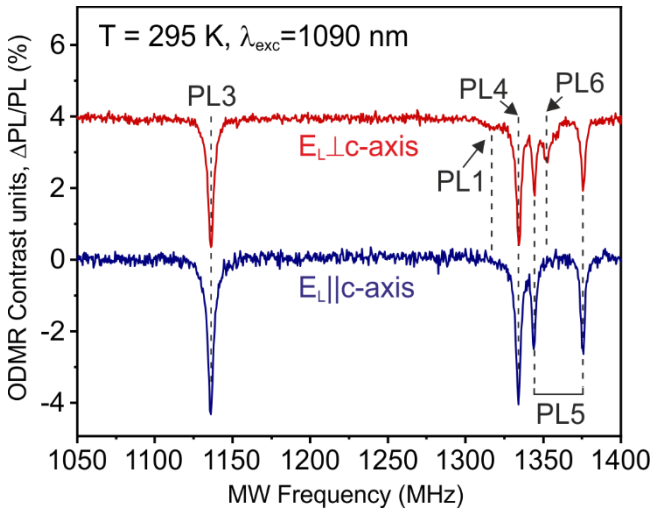

Fig. S2. Room-temperature ODMR spectra of PL1 and PL3 – PL6 excited with laser at 1090 nm (1.137 eV). The spectra illustrate that also at elevated (room) temperature the axial configurations cannot be excited with laser polarization $E_L \| c$, hence their signature is missing in the spectrum obtained with this polarization.

3. Excitation of the divacancy configuration by upconversion processes

When the excitation laser is below the energy of the zero-phonon line (ZPL) of certain defect configuration, direct photon absorption is prohibited by energy conservation. However, in the presence of a phonon bath, the absorption of the photon becomes possible if simultaneously a phonon is destructed supplying its energy to the absorption process, so that the energy conservation law is now satisfied.

$$\hbar\omega_L + \hbar\Omega > E_{ZPL}. \qquad \text{(S1)}$$

Here, $\hbar\omega_L$ denotes the excitation photon energy, $\hbar\Omega$ is the energy of the destructed phonon, and E_{ZPL} is the ZPL energy.

The number of phonons $n(\hbar\Omega)$ of certain energy $\hbar\Omega$ obeys the Planck distribution,

$$n(\hbar\Omega) = (\exp(\hbar\Omega/k_B T) + 1)^{-1}, \quad \text{(S2)}$$

where k_B is the Boltzmann constant and T – the temperature.

Assuming for simplicity that the probability of phonon assisted absorption is proportional to the number of available at certain temperature phonons of energies larger than certain threshold energy $\hbar\Omega_0 = E_{ZPL} - \hbar\omega_L$, we see that the number of suitable phonons and thereby the excitation probability decrease exponentially when the photon energy decreases, because $\hbar\Omega_0$ increases. This is qualitatively illustrated in Fig. S3 showing the room-temperature ODMR spectrum of the sample obtained using several laser energies, from 1.137 eV (1090 nm) down to 1.087 eV (1140 nm). The PL5 and PL6 ODMR lines gradually vanish with decreasing laser energy, and the PL6 vanishes faster due to the larger energy distance between its ZPL and the laser. The PL3 and PL4 lines are well visible in all spectra, albeit the decrease in contrast for both can be noticed with decreasing laser energy due to decreased excitation efficiency.

The upconverted photoluminescence can be monitored directly in the anti-Stokes region of the laser using a double monochromator. This is illustrated in Fig. S4 for two excitation wavelengths, 1089 nm [part (a)] and 1139 nm [part (b)], at several different temperatures. Fig. S4(a) clearly illustrates the appearance of the upconverted PL4 ZPL at a temperature of ~75 K. Fig. S4(b) shows the upconverted ZPLs of PL1, PL2, and PL3, well pronounced at both 100 K and 200 K.

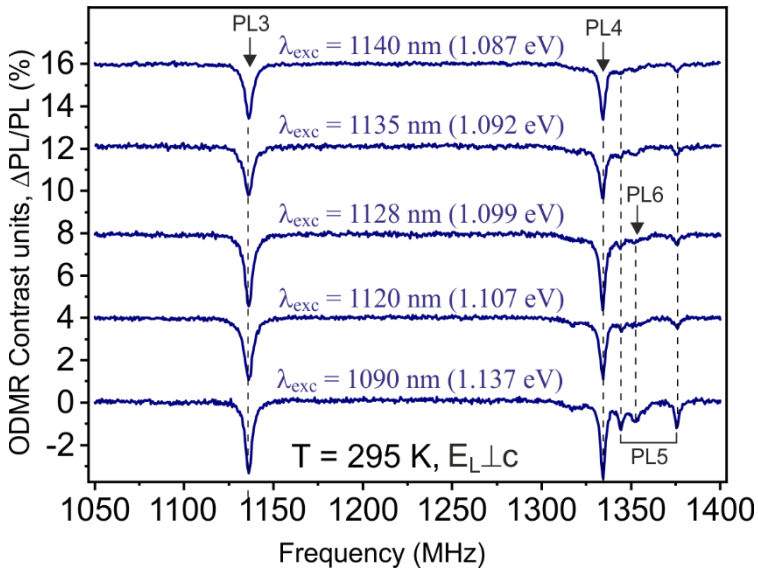

Fig. S3. Continuous wave (CW) ODMR spectra of divacancies in 4H-SiC at room temperature (T = 295 K) obtained with different excitation laser energies. The laser polarization is set to $E_L \perp c$ to excite all divacancy configurations. The spectra are shifted vertically by 4 percent units for better visibility. Except for the laser energy of 1.137 eV (1090 nm), which excites the PL3 configuration directly but is in the anti-Stokes region of PL4, PL5, and PL6, all other laser energies are in the anti-Stokes range of PL3 – PL6 and their observation in ODMR is due to upconversion.

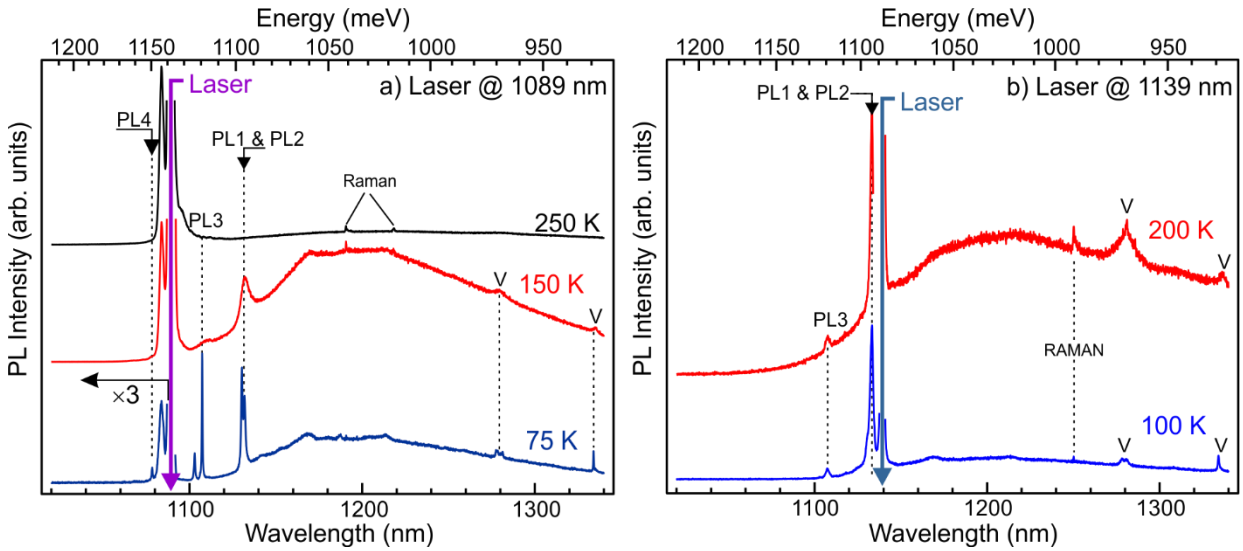

Fig. S4. Upconverted PL spectra in the divacancy region obtained at different temperatures with two laser wavelengths, (a) 1089 nm, and (b) 1139 nm. Different scaling factors are applied to the spectra to promote the details. In panel (a) only the PL4 ZPL is in the anti-Stokes region, while in panel (b) all divacancy lines are in the anti-Stokes region of the laser line. The origin of the peak at 1084 nm is unknown. Vanadium-related emissions can be detected in this sample and are denoted 'V' in the figure. The Raman lines are also marked.

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