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Supplementary Materials for

Anti-Stokes excitation of solid-state quantum emitters for nanoscale thermometry

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Supplementary Information

1. Stokes and Anti-Stokes laser excitation

A quantitative, objective comparison of the Anti-Stokes excitation efficiency for different color centers requires a thoughtful choice of both Anti-Stokes and Stokes excitation lasers. We quantify the Anti-Stokes efficiency by determining the ratio I_{AS}/I_S between the zero phonon line (ZPL) intensity under Anti-Stokes and Stokes excitation. The Anti-Stokes excitation laser is chosen—on the basis of availability—to maximize excitation, and such that its difference in energy with the Stokes one is roughly the same for all investigated color centers. Figure S1 shows, for each color center, the chosen energy for the Anti-Stokes and Stokes excitation lasers with respect to each center's ZPL energy.

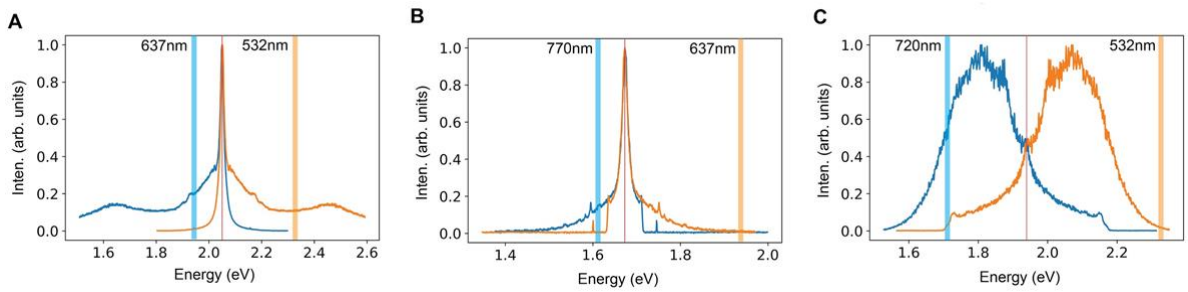

Fig. S1. Emission and absorption spectrum for GeV, SiV, and NV centers. The absorption spectrum shown is simply obtained by reversing the measured emission spectrum with respect to the ZPL. The ZPL energy [red line] as well as the Anti-Stokes [light-blue line] and Stokes [light-ocher line] excitation lasers are shown for each center. The Stokes/Anti-Stokes excitation wavelengths are 532-nm/637-nm for (A), 637-nm/770-nm for (B), and 532-nm/720-nm for (C).

2. Single- vs multi-photon absorption

In the manuscript, we discuss that the observed Anti-Stokes excitation for diamond color centers occurs via absorption of a single low-energy photon assisted by phonon(s)—rather than via nonlinear multi-photon absorption. For one-photon absorption, the emitters fluorescence scales linearly with the excitation intensity integrated over the focal volume, while it scales quadratically for two-photon absorption. Figure S2 displays the fluorescence signal [black data points] measured for GeV centers as a function of input power. The slope of 1 [red curve] on a log-log scale indicates purely linear absorption; note that the fit with a slope of 2 [blue curve]—which would indicate two-photon absorption—is instead inadequate to capture the dynamics of the process.

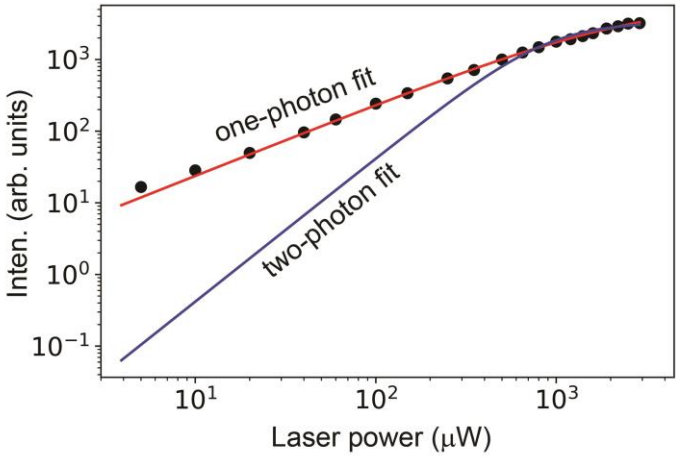

Fig. S2. One- and two-photon absorption fit of the fluorescence signal measured for GeV emitters as a function of input power. The Anti-Stokes excitation wavelength used is 637-nm.

3. Anti-Stokes excitation of SiV centers

In the manuscript we analyze in detail the use of diamond GeV centers for nanothermometry. NV centers were excluded due to their low Anti-Stokes excitation efficiency in our experimental conditions. The GeV center was chosen over the SiV, mainly because of its higher quantum efficiency and better sample availability. Figure S3 shows however that the SiV center displays the same Arrhenius-like behaviour for the intensity of the Anti-Stokes photoluminescence signal with respect to temperature—making it equally suitable to GeV for the nanothermometry scheme we propose.

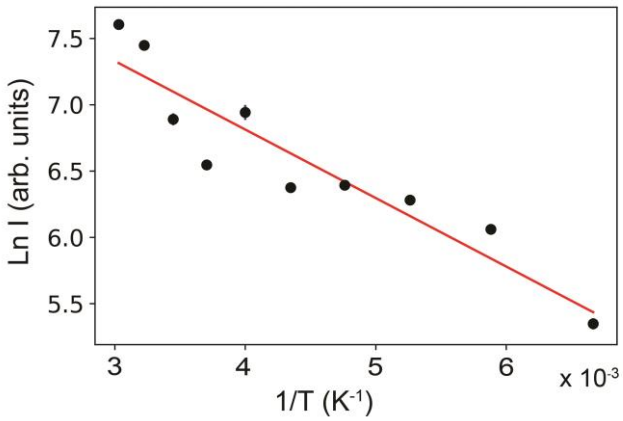

Fig. S3. Temperature dependence of PL intensity signal from SiV centers upon anti-Stokes excitation. The PL intensity was measured monitoring the SiV's ZPL (739 nm) isolated with a bandpass filter. The data is fitted with the Arrhenius-type equation $Ae^{-(E_a/k_BT)}$, where the activation energy E_a = 65.29 meV is fixed to coincide with the difference in energy between the excitation laser and the SiV's ZPL.

4. Atomic force microscopy analysis

The size of different nanodiamonds (NDs) containing GeV, were determined by atomic force microscopy (AFM) (fig. S4). A 400-nm ND containing many GeV centers was chosen to demonstrate

the proposed nanothermometry scheme using Anti-Stokes and Stokes excitation of diamond color centers. Spatial resolution can be improved by selecting smaller ND. In the manuscript (cf. Fig. 2), we show that photoluminescence from a single GeV center upon Anti-Stokes excitation can be measured efficiently.

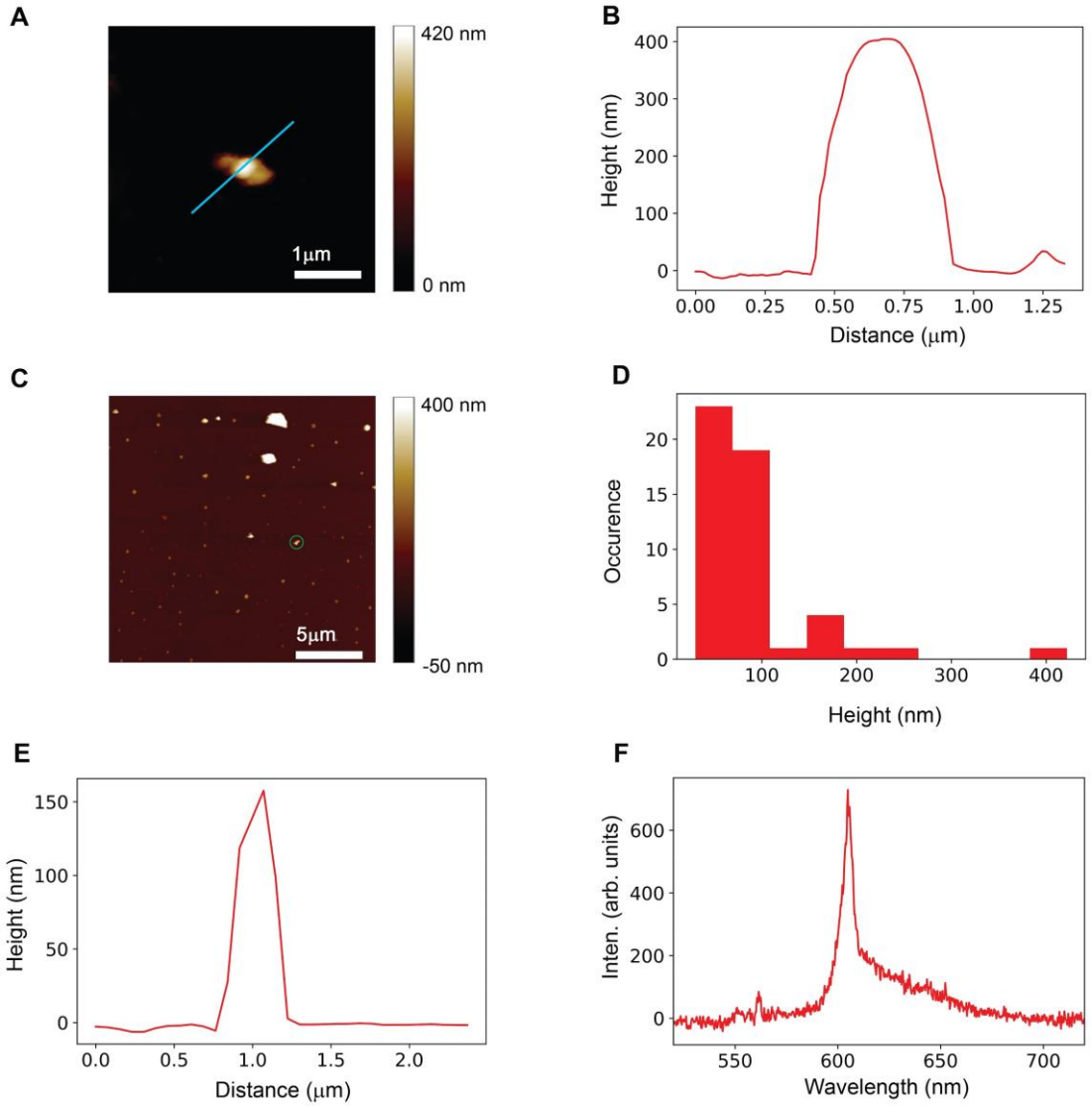

Fig. S4. Summary of some of the physical and optical properties of the nanodiamond sample used in this study. A, B) Atomic force microscopy image (A) and height cross-section analysis (B) of the nanodiamond containing many GeV centers used for Arrhenius analysis and temperature sensing in this study. The size of the nanodiamond is ~400 nm. **C)** AFM scan of a 20×20 μm^2 area chosen to analyze the distribution of heights for several (50) nanodiamonds. **D)** Corresponding histogram showing the nanodiamonds size distribution (most nanodiamonds are ≤100 nm). **E, F)** Most nanodiamonds exhibit detectable photoluminescence: the representative nanodiamond [green circle in C] is ~150 nm in size (E) and shows a prominent GeV PL spectrum (F) under 532-nm excitation at 300-μW (0.26 MW/cm^2) power and 10-s acquisition.

5. Stokes and Anti-Stokes excitation of GeV centers

In the nanothermometry scheme we propose, it is possible to measure temperature variations by directly monitoring the photoluminescence signal I_{AS} under Anti-Stokes excitation (or the equivalent Stokes one I_S). However normalizing the Anti-Stokes PL signal to the Stokes one makes the sensor absolute, i.e. independent of experimental differences. If temperature values were to be determined from I_{AS} alone, any e.g. loss of photons through the surrounding medium would require calibration of the sensor for the experiment specificities. Figure S5 summarizes the independent measurement of I_{AS} and I_S as they vary with temperature.

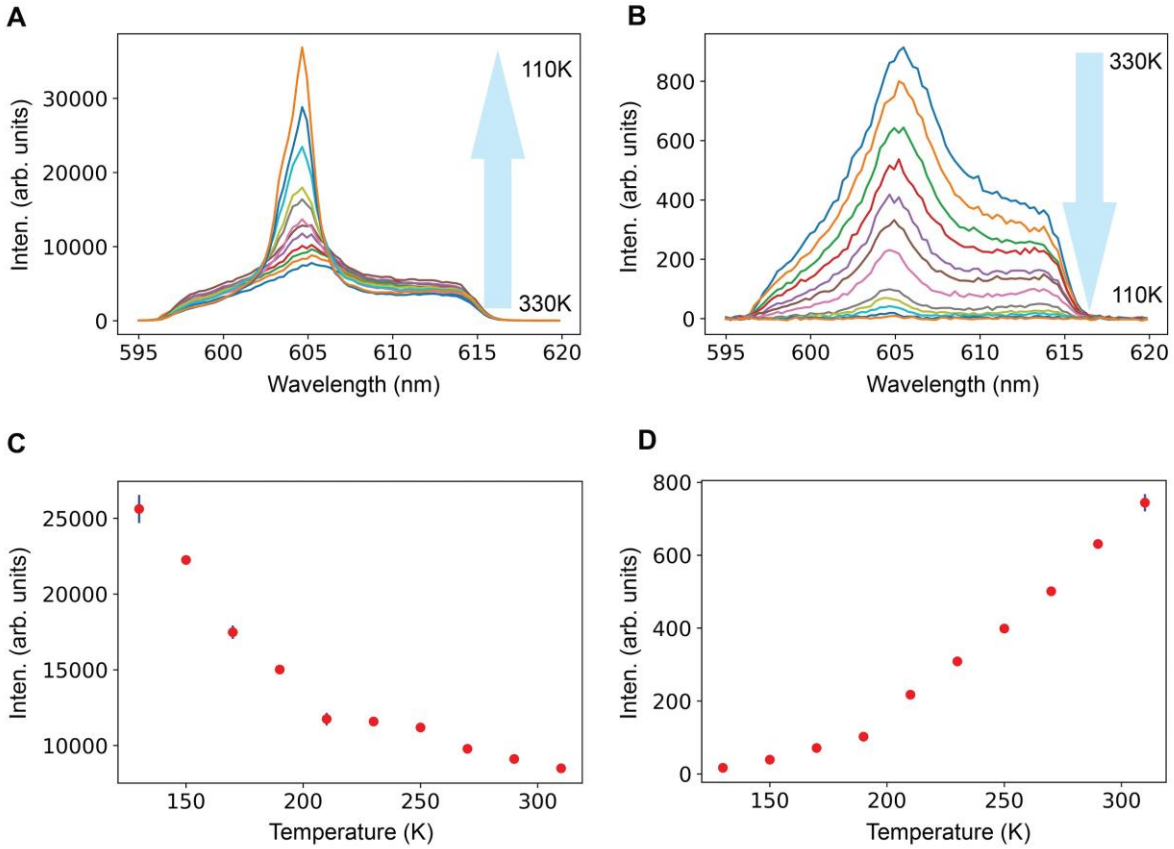

Fig. S5. Overview of the variation with temperature of the PL intensity under Stokes and anti-Stokes excitation. Note how as the temperature increases, the Stokes-PL decreases while the Anti-Stokes-PL increases consistently with an Arrhenius-type dependence. The excitation wavelengths are 532-nm for (A) and (C), and 637-nm for (B) and (D).

6. Confocal maps of Stokes and Anti-Stokes at 298 K and 110 K

The forthwith Anti-Stokes to Stokes difference in PL intensity and its dependence with temperature can be directly visualized in confocal maps (fig. S6).

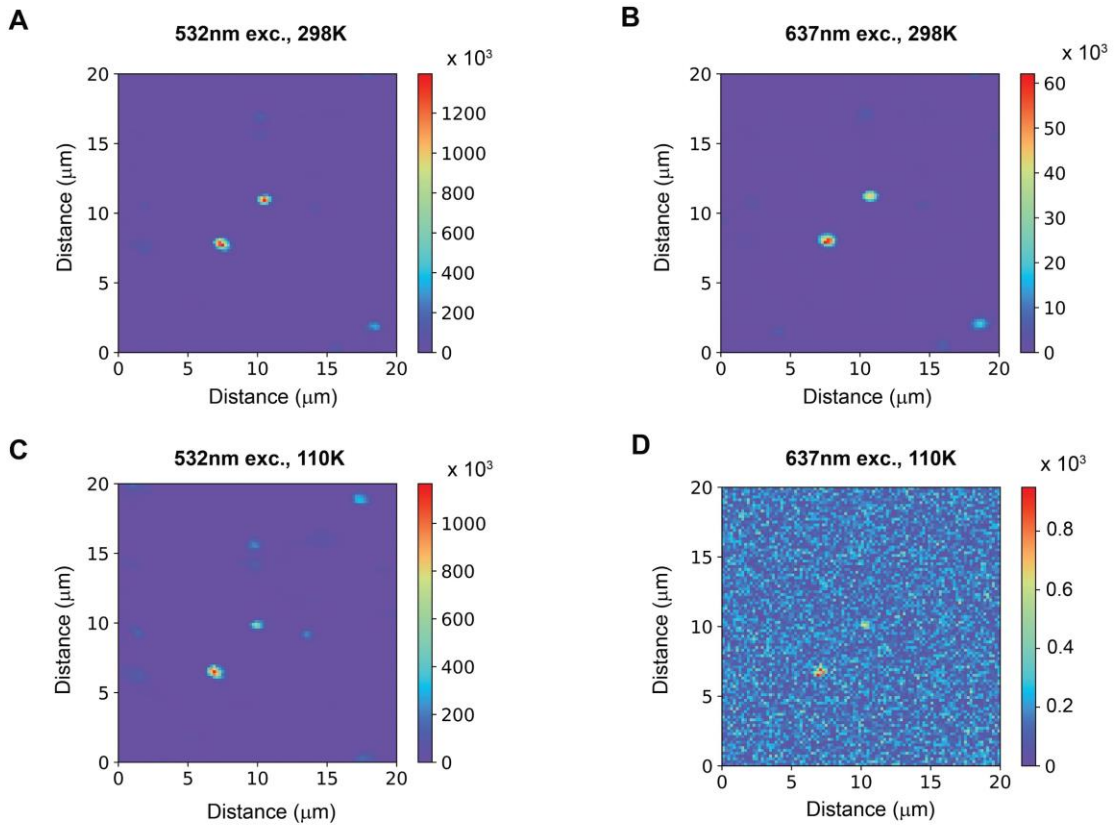

Fig. S6. Confocal maps of a 20 μm × 20 μm showing the PL signal from isolated nanodiamonds containing many GeV centers. The maps highlight the comparison in PL intensity under Stokes (532 nm) and Anti-Stokes (637 nm) excitation at 298 K (A, B) and at 110 K (C, D).

7. Noise-floor determination for thermometry

As we mention in the manuscript, resolution is a relative quantity and can be improved. To account for the lack of an absolute determination, the standard practice is to express the resolution in $K \cdot Hz^{-½}$, which establishes the value of the resolution for a 1-second signal acquisition.

In our case, the noise of the photoluminescence signal on the detector—determined as the standard deviation of the measured noise-floor with a 1-s bandwidth—is taken as the measure of the minimum resolvable signal (for the specified 1-s bandwidth). This is then converted to the corresponding value of minimum resolvable (i.e. noise-floor) temperature through the PL intensity Anti-Stokes to Stokes ratio.