

# Fluorescence thermometry enhanced by the quantum coherence of single spins in diamond

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**We demonstrate fluorescence thermometry techniques with sensitivities approaching 10 mK·Hz<sup>-1/2</sup> based on the spin-dependent photoluminescence of nitrogen vacancy (NV) centers in diamond. These techniques use dynamical decoupling protocols to convert thermally induced shifts in the NV center's spin resonance frequencies into large changes in its fluorescence. By mitigating interactions with nearby nuclear spins and facilitating selective thermal measurements, these protocols enhance the spin coherence times accessible for thermometry by 45-fold, corresponding to a 7-fold improvement in the NV center's temperature sensitivity. Moreover, we demonstrate these techniques can be applied over a broad temperature range and in both finite and near-zero magnetic field environments. This versatility suggests that the quantum coherence of single spins could be practically leveraged for sensitive thermometry in a wide variety of biological and microscale systems.**

spintronics | electron spin resonance | quantum control

Thermometry based on thermally driven changes in fluorescence lifetimes or intensities is an essential technique in many environments that preclude electrical probes (1). Although typical fluorescence thermometers use millimeter-scale optical probes (2), the desire to noninvasively monitor intracellular thermal gradients has motivated efforts to develop analogous methods at the nanoscale (3, 4). This interest has stimulated the development of nanoscale fluorescence thermometers based on quantum dots (5), rare-earth ions (6), and nanogels (7), with recent studies suggesting that intracellular temperature gradients are on the order of 1 K (8). However, the application of conventional fluorescence thermometry techniques in biological settings is limited by temperature resolutions of ~0.2 K or worse (8–10), motivating the development of more advanced nanoscale thermometers.

In recent years, solid-state electronic spins have gained considerable attention for applications in nanoscale sensing. In particular, the diamond nitrogen vacancy (NV) center (Fig. 1A) has garnered attention for its optical spin initialization and fluorescence-based spin readout (11), the ability to isolate and measure single defects (12), and the ability to manipulate its spin using microwave electron spin resonance techniques (13). NV center sensing is based on monitoring shifts in the spin resonance frequencies through the defect's fluorescence as a function of external perturbations such as magnetic fields (14–17), electric fields (18), or temperature (19, 20), with the sensitivity of these techniques scaling as  $1/\sqrt{T_C}$ , where  $T_C$  is the relevant spin coherence time (21). These coherence times can be enhanced by two to three orders of magnitude for perturbations amenable to time-periodic (AC) modulation through the use of dynamical decoupling techniques that periodically invert the spin state and the signal being sensed to mitigate the effects of low-frequency magnetic noise (22–24). These methods have enabled the detection of single electronic spins (15) and nanoscale nuclear spin ensembles external to the diamond (16, 17), with motivations to extend these techniques to biological systems using NV centers in nanodiamonds (25).

Here we demonstrate that the quantum coherence of a single NV center can enhance thermometry. Our technique relies on

the use of dynamical decoupling protocols that manipulate the NV center's spin-one ground state to selectively measure thermally driven shifts in the spin resonance frequencies while suppressing the effects of low-frequency magnetic noise. This allows us to exploit the NV center's long spin coherence for thermometry. We achieve spin coherence times for thermal sensing exceeding 80  $\mu$ s, resulting in inferred thermal sensitivities of 25 mK·Hz<sup>-1/2</sup>. By combining these prolonged coherence times with improved fluorescence detection (26), we estimate that thermal sensitivities better than 10 mK·Hz<sup>-1/2</sup> should be achievable. These sensitivities demonstrate the NV center's potential to markedly improve on the ~0.2-K temperature resolution offered by competing nanoscale fluorescence thermometry techniques (3, 4, 8–10). We execute these measurements in two regimes: in moderate magnetic fields where both spin transitions can be resonantly addressed with separate microwave signals and near zero magnetic field where they can be addressed with a single microwave frequency. Finally, we demonstrate the wide range of operating temperatures for NV center thermometers by performing these measurements at 500 K. Together, these results provide a robust set of protocols for NV center-based thermometry.

## Principles of Spin-Based Fluorescence Thermometry

Our work focuses on the precise measurement of the NV center's temperature-dependent crystal field splitting ( $D$ ) between its  $m_S = 0$  and  $m_S = \pm 1$  sublevels, as seen in the ground-state spin Hamiltonian (27):

$$H_{\text{NV}} = DS_z^2 + g\mu_B\vec{B}\vec{S} + \vec{S}\vec{A}\vec{I}. \quad [1]$$

Here  $\vec{S}$  is the electronic spin operator,  $g = 2.00$  is the electron  $g$  factor,  $\mu_B$  is the Bohr magneton,  $\vec{B}$  is the applied magnetic field,  $\vec{A}$  is the hyperfine tensor, and  $\vec{I}$  is the nitrogen nuclear spin operator ( $I = 1$ ). Additional considerations regarding Eq. 1, such as the influence of strain and electric fields, are discussed in *SI Appendix*. The crystal field splitting, ~2.870 GHz at room temperature, exhibits shifts of ~74 kHz/K due to thermal expansion (20) and vibronic interactions (28). Because the  $D$  term is second order in  $S_z$ , ground-state-level shifts due to changes in temperature can be distinguished from Zeeman shifts (Fig. 1B). This point has recently been used to perform NV center magnetometry that is insensitive to temperature drift (29). Here we take the opposite approach to perform thermometry that is robust against the NV center's interactions with its magnetic environment. Our approach is to resonantly manipulate the spin such that at

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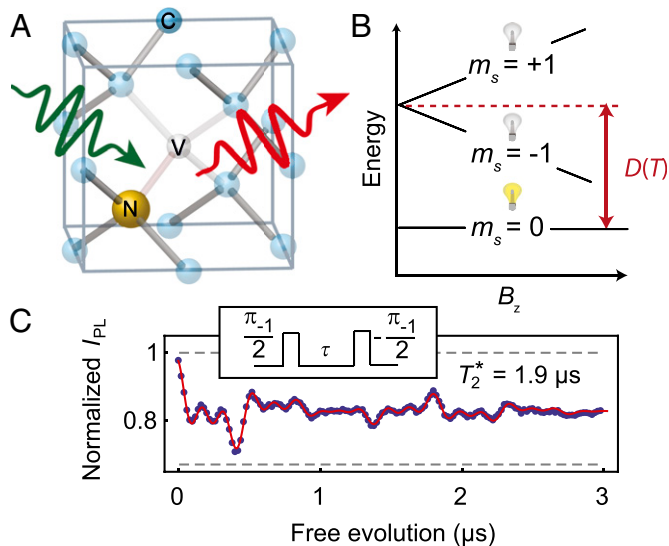
The authors declare no conflict of interest.

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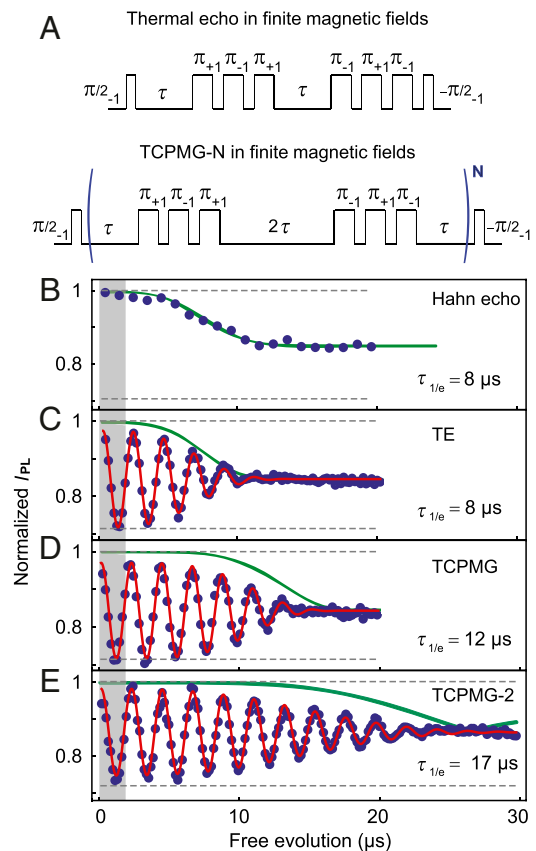
**Fig. 1.** Nitrogen vacancy center in diamond. (A) Depiction of a nitrogen vacancy (NV) center in the diamond lattice. The wavy green arrow represents the 532-nm laser used for optical excitation and the wavy red arrow represents the phonon-broadened fluorescence used to measure the spin state. (B) Fine structure of the NV center ground state as a function of axial magnetic field. The light bulbs represent the relative fluorescence difference for the  $m_S = 0$  and  $m_S = \pm 1$  states. Temperature changes shift the crystal field splitting ( $D$ ), whereas magnetic fields ( $B_z$ ) split the  $m_S = \pm 1$  sublevels. This difference enables dynamical decoupling pulse sequences that move the spin between all three states to selectively measure temperature shifts and mitigate magnetic noise. (C) Ramsey measurement performed on the  $m_S = 0$  to  $m_S = -1$  transition ( $B_z = 40$  G). Inset illustrates the pulse sequence. The short inhomogeneous spin lifetime ( $T_2^*$ ) limits the sensitivity of conventional NV center thermometry. The uncertainties in  $I_{PL}$  estimated from the photon shot noise, are  $\sim 0.003$ . The microwave carrier frequency was detuned from the  $m_l = 0$  hyperfine resonance by  $\sim 3.5$  MHz to induce oscillations in  $I_{PL}$ . The fluorescence signal exhibits a beating caused by the three hyperfine resonances and weak coupling to a nearby  $^{13}\text{C}$  spin. Gray dashed lines show the fluorescence intensity of  $m_S = 0$  and  $m_S = -1$  as determined by independent measurements.

specific times the relative phase of the spin states in the laboratory frame becomes  $e^{-iDt}$ , where  $t$  is the spin's total free evolution time. As this phase is independent of the magnetic field (up to fluctuations on the timescale of the interpulse delay,  $\tau$ ), it is protected from the low-frequency magnetic fluctuations that limit the coherence to the inhomogeneous spin lifetime ( $T_2^*$ ). Similarly, the phase is independent of the nitrogen nuclear spin state, thus eliminating interference effects observed with conventional Ramsey measurement techniques used to sense static (DC) shifts in the resonance frequencies (Fig. 1C). This relative phase is then converted into a population difference of the spin sublevels and measured through the fluorescence intensity ( $I_{PL}$ ). The fluorescence is  $\sim 30\%$  greater for the  $m_S = 0$  state than for the  $m_S = \pm 1$  states, and varies linearly with the  $m_S = 0$  spin population, providing a direct measurement of the NV center spin. This measurement sequence is repeated until the desired level of  $I_{PL}$  is reached. As a function of  $t$ , the  $I_{PL}$  signal oscillates between  $I_{PL}(m_S = 0)$  and  $I_{PL}(m_S = \pm 1)$  with a frequency given by  $D - \Omega_{\text{REF}}$ , where  $\Omega_{\text{REF}}$  corresponds to the microwave carrier frequencies used for spin manipulation. Small thermally driven changes in  $D$  (as well as the value of  $D$  itself) can therefore be measured through large changes in the NV center's fluorescence.

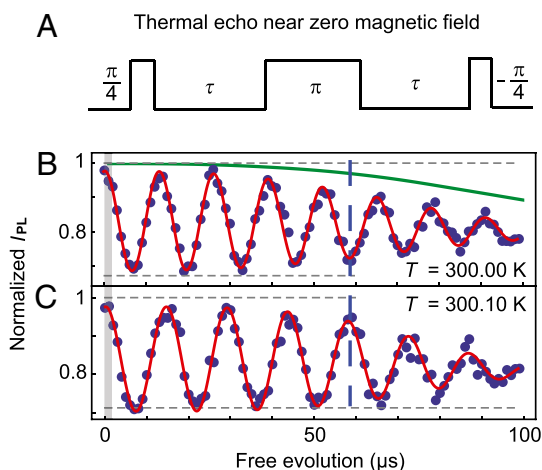
### Fluorescence Thermometry in Finite Magnetic Fields

We first demonstrate “thermal” analogs to conventional Hahn echo and Carr–Purcell–Meiboom–Gill (CPMG–N) pulse sequences (30) in finite magnetic fields, where both the  $m_S = 0$  to  $m_S = -1$  and  $m_S = 0$  to  $m_S = +1$  transitions are resonantly

addressed. After optically initializing the spin into the  $m_S = 0$  sublevel with a 2- $\mu\text{s}$  laser pulse, we apply one of the pulse sequences shown in Fig. 2A, referred to here as the thermal echo (TE) and thermal CPMG–N (TCPMG–N). These pulse sequences follow the same general methodology: The spin is first initialized into a superposition of two of its three eigenstates and then undergoes periods of free evolution punctuated by operations of the form  $\pi_{+1}\pi_{-1}\pi_{+1}$  or  $\pi_{-1}\pi_{+1}\pi_{-1}$ , where the subscripts indicate the spin transition being addressed; e.g.,  $\pi_{-1}$  acts on the  $m_S = 0$  to  $m_S = -1$  transition. These operations interchange the spin populations in the  $m_S = +1$  and  $m_S = -1$  states, thus inverting the NV center spin state. As a result of the inversions, the  $m_S = +1$  and  $m_S = -1$  states acquire a total phase  $e^{-iDt}$ , which is independent of static magnetic fields and low-frequency magnetic noise. The final microwave pulse converts this phase into



**Fig. 2.** Thermal echo (TE) and thermal CPMG–N (TCPMG–N) pulse sequences in finite magnetic fields. (A) Diagram showing the pulse sequences. Here a  $\pi$  pulse has a duration such that it will invert the spin population between the two sublevels that are resonantly addressed. The subscripts indicate the two sublevels that are resonantly addressed. (B) Hahn echo measurement ( $m_S = 0$  to  $m_S = -1$  transition) at  $B_z = 30$  G showing  $I_{PL}$  as a function of the free evolution time ( $2\tau$  for the Hahn echo and TE,  $4\tau$  for TCPMG, and  $8\tau$  for TCPMG–2). The measurement demonstrates the coherence collapse caused by the incoherent precession of the  $^{13}\text{C}$  spin bath. The width of the shaded gray region represents  $T_2^*$ . C, D, and E show TE, TCPMG, and TCPMG–2 measurements, respectively, performed at 297.00 K (SI Appendix). The uncertainties in  $I_{PL}$  estimated from the photon shot noise, are  $\sim 0.005$ . To induce oscillations in  $I_{PL}$  to clearly observe the signal envelope, the average microwave carrier frequency ( $\Omega_{\text{REF}}$ ) was detuned from  $D$  by  $\sim 0.5$  MHz. The solid red lines are best fits to the data and the  $1/e$  decay times ( $\tau_{1/e}$ ) are noted on the plots. The observed coherences are in good agreement with numerical modeling (solid green lines). For the TCPMG–2 sequence the coherence time is ninefold greater than  $T_2^*$ . For these experimental conditions we infer the thermal sensitivity ( $\eta$ ) is  $54 \pm 1$  mK·Hz $^{-1/2}$ . Enhancements in the photon collection efficiency could improve  $\eta$  to  $\sim 15$  mK·Hz $^{-1/2}$  (Methods).



**Fig. 3.** Thermal echo sequence near zero magnetic field. (A) Diagram showing the thermal echo pulse sequence near zero magnetic field when the frequency separation of the  $m_S = \pm 1$  sublevels is less than the bandwidth of the microwave pulse used to address the transitions (25 MHz). Here a  $\pi$  pulse has a duration such that the spin, initialized into  $m_S = 0$ , goes through a superposition of the  $m_S = \pm 1$  states and returns to  $m_S = 0$  with an opposite sign. (B) Thermal echo measurement at 300.00 K. The microwave carrier frequency ( $\Omega_{\text{REF}}$ , 2.87016 GHz) was detuned from  $D$  by  $\sim 75$  kHz to induce oscillations in the signal to observe the coherence envelope. The solid green line shows the coherence predicted by the numerical modeling. The width of the shaded gray region represents  $T_2^*$ . (C) The same measurement as in B, but with the sample temperature at 300.10 K. The shift in  $D$  results in a pronounced difference in the signal frequency, leading to large  $I_{\text{PL}}$  differences at long times (dashed blue line). For both measurements  $\tau_{1/e}$  is  $\sim 85$   $\mu\text{s}$ , and the uncertainties in  $I_{\text{PL}}$ , estimated from the photon shot noise, are  $\sim 0.02$ . For reference, for these data the measurement time per point was 50 s. From the observed coherence times we infer  $\eta = 25 \pm 2$   $\text{mK}\cdot\text{Hz}^{-1/2}$  for these experimental conditions; we estimate that enhanced photon collection efficiencies could improve  $\eta$  to  $\sim 7$   $\text{mK}\cdot\text{Hz}^{-1/2}$ . The frequency difference for the oscillations in B and C, inferred from the fits, is  $8 \pm 2$  kHz, in good agreement the expected value,  $\sim 7.4$  kHz (20).

a population of the  $m_S = 0$  state, which is measured optically. The key difference between the TE and the TCPMG-N sequences is that the TCPMG-N sequences invert the spin more frequently (2N times) and thus counteract higher-frequency magnetic noise. Note that the final  $\pi_{-1}\pi_{+1}\pi_{-1}$  operation in the TE sequence compensates for undesired phases acquired during the duration of the  $\pi$  pulses and the interpulse delays (see *SI Appendix* for further details). The TCPMG-N sequences also include two symmetrized  $\pi_{-1}\pi_{+1}\pi_{-1}$  operations per period, compensating for these undesired phase accumulations and providing better protection from noise (31).

We apply these pulse sequences to a single NV center in a diamond with natural  $^{13}\text{C}$  abundance (1.1%) in a magnetic field ( $B_z = 30$  G). In these materials the  $^{13}\text{C}$  nuclear spins ( $I = 1/2$ ) are the primary source of decoherence, limiting  $T_2^*$  to a few microseconds. Conventional Hahn echo measurements can extend the coherence to hundreds of microseconds, but are limited by the incoherent precession of the  $^{13}\text{C}$  nuclei, which causes the coherence to collapse and revive at the  $^{13}\text{C}$  Larmor frequency (32). Previous studies demonstrated that dynamical decoupling sequences, such as CPMG-N, can counteract the  $^{13}\text{C}$  precession to maintain coherence over significantly enhanced timescales (23), and here we demonstrate that this coherence can be accessed for DC thermal sensing. Our focus is on extending the timescale of the first coherence collapse, because our three-level pulse protocols lead to three incommensurate  $^{13}\text{C}$  precession frequencies that do not produce the coherence revivals observed in the two-level Hahn echo (33). Fig. 2B shows the Hahn echo

coherence, with the width of the gray shaded region corresponding to the spin's  $T_2^*$ . The TE sequence achieves a coherence time similar to that of the Hahn echo sequence, approximately four times greater than  $T_2^*$  (Fig. 2C). The TCPMG (Fig. 2D) and TCPMG-2 (Fig. 2E) sequences extend the spin coherence even further in time. The coherence time reaches 17.6  $\mu\text{s}$  for TCPMG-2, corresponding to a ninefold improvement in coherence over  $T_2^*$  and a threefold improvement in thermal sensitivity ( $\eta$ ) compared with a Ramsey measurement. Using Eq. 4 described in *Methods*, which is based on monitoring thermally driven changes in  $I_{\text{PL}}$  at the free evolution time that mutually optimizes the coherence and accumulated phase, we infer that for these experimental parameters  $\eta = 54 \pm 1$   $\text{mK}\cdot\text{Hz}^{-1/2}$ . Combining our observed coherence with higher photon collection efficiencies achieved in scanning diamond magnetometers (34) could improve  $\eta$  to  $\sim 15$   $\text{mK}\cdot\text{Hz}^{-1/2}$ .

Our measurements show good agreement with the results of numerical modeling for the spin dynamics of an NV center in a  $^{13}\text{C}$  spin bath subjected to the TE and TCPMG-N sequences (solid green lines in Fig. 2B–E; see *Methods* for further details). We note that the difference between the modeling results and the experimental data is larger for the sequences involving more pulses, suggesting that they are caused by pulse imperfections. Interestingly, the simulations for TCPMG-2 (Fig. 2E) show a distinct feature near 25  $\mu\text{s}$ , when the coherence collapses and then revives with a  $180^\circ$  shift in phase in the oscillations. We have observed similar behavior on other NV centers in our diamond sample (*SI Appendix*) and tentatively attribute these features to coupling to the most proximal  $^{13}\text{C}$  nuclei (32). The overall correspondence between the coherence observed in the measurements and that observed in the numerical simulations supports the assertion that the  $^{13}\text{C}$  nuclear spins are a primary limiting factor for these measurements. These observations suggest that the  $^{13}\text{C}$  dynamics could be further suppressed to produce improved thermal sensitivities not only through the application of higher-order TCPMG-N sequences, but also by reducing the magnetic field to lower the  $^{13}\text{C}$  precession frequency.

### Fluorescence Thermometry Near Zero Magnetic Field

Near zero magnetic field, the bandwidth of the resonant microwave pulses exceeds the spectral width of the  $m_S = +1$  and  $m_S = -1$  resonances, and the thermal echo can be performed with a single microwave source (Fig. 3A). We consider near zero magnetic fields ( $B_z \sim 0.5$  G) to mitigate mixing of the  $m_S = \pm 1$  states induced by transverse strain (18). In this limit the TE sequence has an analogous form to that of pulse sequences proposed for NV center timekeeping (35), where the  $\pi$  pulse that inverts the spin state has a duration such that a spin initially in  $m_S = 0$  goes through a superposition of  $m_S = \pm 1$  and returns to  $m_S = 0$  with an opposite sign.

In this small magnetic field, the TE sequence produces a longer coherence time of  $\sim 85$   $\mu\text{s}$  (Fig. 3B), in good agreement with numerical simulations. This improves the inferred  $\eta$  to  $25 \pm 2$   $\text{mK}\cdot\text{Hz}^{-1/2}$  for these measurements and we estimate that improved fluorescence detection techniques could improve  $\eta$  to  $\sim 7$   $\text{mK}\cdot\text{Hz}^{-1/2}$ . To show the sensitivity of this coherence to temperature shifts, we perform a direct experimental demonstration where we increase the temperature of the diamond substrate by 0.1 K while keeping the microwave carrier frequency ( $\Omega_{\text{REF}}$ ) fixed (Fig. 3C). The change in the accumulated phase of the  $m_S = +1$  and  $m_S = -1$  states produces a pronounced change in the  $I_{\text{PL}}$  signal—the dashed blue line spanning Fig. 3B and C draws attention to when the two signals have opposite phase. As the 0.1-K shift is clearly resolved, these measurements demonstrate that NV centers could offer a significant improvement in thermal sensitivity relative to alternative nanoscale fluorescence thermometers (3, 4, 8–10). Even longer coherence times approaching  $\sim 1$  ms, achieved through the application of higher-order decoupling sequences or the use of isotopically purified



7. Gota C, Okabe K, Funatsu T, Harada Y, Uchiyama S (2009) Hydrophilic fluorescent nanogel thermometer for intracellular thermometry. *J Am Chem Soc* 131(8):2766–2767.
8. Okabe K, et al. (2012) Intracellular temperature mapping with a fluorescent polymeric thermometer and fluorescence lifetime imaging microscopy. *Nat Commun* 3:705.
9. Donner JS, Thompson SA, Kreuzer MP, Baffou G, Quidant R (2012) Mapping intracellular temperature using green fluorescent protein. *Nano Lett* 12(4):2107–2111.
10. Yang JM, Yang H, Lin LW (2011) Quantum dot nano thermometers reveal heterogeneous local thermogenesis in living cells. *ACS Nano* 5(6):5067–5071.
11. van Oort E, Manson NB, Glasbeek M (1988) Optically detected spin coherence of the diamond N-V centre in its triplet ground state. *J Phys Chem* 21(23):4385–4391.
12. Gruber A, et al. (1997) Scanning confocal optical microscopy and magnetic resonance on single defect centers. *Science* 276(5321):2012–2014.
13. Jelezko F, et al. (2004) Observation of coherent oscillation of a single nuclear spin and realization of a two-qubit conditional quantum gate. *Phys Rev Lett* 93(13):130501.
14. Hong S, et al. (2013) Nanoscale magnetometry with NV centers in diamond. *MRS Bull* 38(02):155–161.
15. Grinolds MS, et al. (2013) Nanoscale magnetic imaging of a single electron spin under ambient conditions. *Nat Phys* 9(4):215–219.
16. Mamin HJ, et al. (2013) Nanoscale nuclear magnetic resonance with a nitrogen-vacancy spin sensor. *Science* 339(6119):557–560.
17. Staudacher T, et al. (2013) Nuclear magnetic resonance spectroscopy on a (5-nanometer)<sup>3</sup> sample volume. *Science* 339(6119):561–563.
18. Dolde F, et al. (2011) Electric-field sensing using single diamond spins. *Nat Phys* 7(6):459–463.
19. Toyli DM, et al. (2012) Measurement and control of single nitrogen-vacancy center spins above 600 K. *Phys Rev X* 2(3):031001.
20. Acosta VM, et al. (2010) Temperature dependence of the nitrogen-vacancy magnetic resonance in diamond. *Phys Rev Lett* 104(7):070801.
21. Taylor JM, et al. (2008) High-sensitivity diamond magnetometer with nanoscale resolution. *Nat Phys* 4(10):810–816.
22. de Lange G, Wang ZH, Risté D, Dobrovitski VV, Hanson R (2010) Universal dynamical decoupling of a single solid-state spin from a spin bath. *Science* 330(6000):60–63.
23. Ryan CA, Hodges JS, Cory DG (2010) Robust decoupling techniques to extend quantum coherence in diamond. *Phys Rev Lett* 105(20):200402.
24. Naydenov B, et al. (2011) Dynamical decoupling of a single-electron spin at room temperature. *Phys Rev B* 83(8):081201.
25. McGuinness LP, et al. (2011) Quantum measurement and orientation tracking of fluorescent nanodiamonds inside living cells. *Nat Nanotechnol* 6(6):358–363.
26. Babinec TM, et al. (2010) A diamond nanowire single-photon source. *Nat Nanotechnol* 5(3):195–199.
27. Loubser JHN, van Wyk JA (1978) Electron spin resonance in the study of diamond. *Rep Prog Phys* 41(8):1201–1248.
28. Doherty MW, et al. (2013) The nitrogen-vacancy colour centre in diamond. *Phys Rep*, 10.1016/j.physrep.2013.1002.1001.
29. Fang K, et al. (2013) High-sensitivity magnetometry based on quantum beats in diamond nitrogen-vacancy centers. *Phys Rev Lett* 110:130802.
30. Slichter CP (1990) *Principles of Magnetic Resonance* (Springer, New York), 3rd Ed.
31. Haeberlen U (1976) *High Resolution NMR in Solids: Selective Averaging* (Academic, New York).
32. Childress L, et al. (2006) Coherent dynamics of coupled electron and nuclear spin qubits in diamond. *Science* 314(5797):281–285.
33. Reinhard F, et al. (2012) Tuning a spin bath through the quantum-classical transition. *Phys Rev Lett* 108(20):200402.
34. Maletinsky P, et al. (2012) A robust scanning diamond sensor for nanoscale imaging with single nitrogen-vacancy centres. *Nat Nanotechnol* 7(5):320–324.
35. Hodges JS, et al. (2013) Timekeeping with electron spin states in diamond. *Phys Rev A* 87:032118.
36. Balasubramanian G, et al. (2009) Ultralong spin coherence time in isotopically engineered diamond. *Nat Mater* 8(5):383–387.
37. Jarmola A, Acosta VM, Jensen K, Chemersov S, Budker D (2012) Temperature- and magnetic-field-dependent longitudinal spin relaxation in nitrogen-vacancy ensembles in diamond. *Phys Rev Lett* 108(19):197601.
38. Majumdar A, et al. (1995) Thermal imaging by atomic-force microscopy using thermocouple cantilever probes. *Rev Sci Instrum* 66(6):3584–3592.
39. Hodges JS, et al. (2012) Long-lived NV- spin coherence in high-purity diamond membranes. *New J Phys* 14:093004.
40. Ohno K, et al. (2012) Engineering shallow spins in diamond with nitrogen delta-doping. *Appl Phys Lett* 101:082413.
41. Horowitz VR, Alemán BJ, Christle DJ, Cleland AN, Awschalom DD (2012) Electron spin resonance of nitrogen-vacancy centers in optically trapped nanodiamonds. *Proc Natl Acad Sci USA* 109(34):13493–13497.
42. Geiselmann M, et al. (2013) Three-dimensional optical manipulation of a single electron spin. *Nat Nanotechnol* 8(3):175–179.
43. Dobrovitski VV, Feiguin AE, Awschalom DD, Hanson R (2008) Decoherence dynamics of a single spin versus spin ensemble. *Phys Rev B* 77(24):245212.
44. Neumann P, et al. (2013) High precision nanoscale temperature sensing using single defects in diamond. arXiv:1304.0688.
45. Kucsko G, et al. (2013) Nanometer scale quantum thermometry in a living cell. arXiv:1304.1068.