Room-temperature entanglement between single defect spins in diamond

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Entanglement is the central yet fleeting phenomenon of quantum physics. Once being considered a peculiar counter-intuitive property of quantum theory\textsuperscript{1}, it has developed into the most central element of quantum technology. Consequently, there have been a number of experimental demonstrations of entanglement between photons\textsuperscript{2}, atoms\textsuperscript{3}, ions\textsuperscript{4} and solid-state systems such as spins or quantum dots\textsuperscript{5,7}, superconducting circuits\textsuperscript{8,9} and macroscopic diamond\textsuperscript{10}. Here we experimentally demonstrate entanglement between two engineered single solid-state spin quantum bits (qubits) at ambient conditions. Photon emission of defect pairs reveals ground-state spin correlation. Entanglement (fidelity = 0.67 ± 0.04) is proved by quantum state tomography. Moreover, the lifetime of electron spin entanglement is extended to milliseconds by entanglement swapping to nuclear spins. The experiments mark an important step towards a scalable room-temperature quantum device being of potential use in quantum information processing as well as metrology.

Engineering entangled quantum states is a decisive step in quantum technology. Although entanglement among weakly interacting systems such as photons has been demonstrated already in the early stages of quantum optics, deterministic generation of entanglement in more complex systems such as atoms or ions, not to mention solids, is a relatively recent achievement\textsuperscript{11}. Usually in solid-state systems rapid dephasing causes any useful degree of quantum correlations. Either decoupling must be used to protect quantum states or careful materials engineering is required to prolong coherence. Most often however, and this is especially important for solid-state systems, one needs to resort to low (milliKelvin) temperatures to achieve sufficiently robust and long-lasting quantum coherence. Spins are sufficiently weakly coupled to their environment to allow for the observation of coherence at room temperatures.

Diamond defect spins are particularly interesting solid-state spin qubit systems. A number of hallmark demonstrations such as single-, two- and three-qubit operations, high-fidelity single-shot readout\textsuperscript{12}, one- and two-qubit algorithms\textsuperscript{13}, and entanglement between nuclear and electron and nuclear spin qubits have been achieved\textsuperscript{14}. Different schemes to scale the system to a larger number of entangled electron spins have been proposed\textsuperscript{15–17}. A path towards room-temperature entanglement is strong coupling among the ground-state spin magnetic dipole moment of adjacent defects centres. This mutual dipolar interaction scales as distance $d^{-3}$ and should be larger than the interaction of each electron spin with the residual paramagnetic impurities or nuclear spin moments in the lattice (Fig. 1d). Typical cutoff distances for strong interaction are thus limited by the electron spin dephasing time (milliseconds) to be around 30 nm. Here we demonstrate entanglement between two electron and nuclear spins at a distance of approximately 25 nm. At these distances magnetic dipole coupling is strong enough to attain high-fidelity entanglement while being able to address the spins individually by super-resolution optical microscopy\textsuperscript{18}.

The optical as well as spin physics of nitrogen vacancy (NV) defects in diamond has been subject to numerous investigations\textsuperscript{11,19}. The optical intensity of the strongly allowed optical transition between ground and excited spin triplet states depends on the magnetic quantum number of the ground state and it is larger for $m_S = 0$ and smaller for $m_S = \pm 1$, allowing optical read-out of the electron spin\textsuperscript{10}. The coherence time $T_2$ of the NV$^-$ electron spin depends on the concentration of $^{13}$C spins and reaches up to 3 ms for $^{12}$C enriched diamond\textsuperscript{11}.

To generate strongly coupled defect pairs with high probability and at the same time optimum decoherence properties, we have implanted nitrogen ions ($^{14}$N$^+$) with kinetic energies of 1 MeV, corresponding to an implantation depth of 730 nm using a 10-μm-thick mica nano-aperture mask (hole diameter 20 nm). This process creates NV pairs at distances less than 20 nm with a success rate of 2% (see Supplementary Information)\textsuperscript{21}.

Figure 1b shows the spin energy levels of the NV pair together with the optically detected electron spin resonance spectrum of two coupled electron spins. The spectrum in secular approximation is described by

$$H = \sum_{i=A}^{B} (S_i \cdot D + \gamma_e B S_i) + \nu_{\text{dip}} S_{iA} S_{iB}$$

(1)

where $D$ is the zero field splitting or fine structure, $B$ is the magnetic field, $\gamma_e$ is the gyromagnetic ratio and $S_{iA}$ is the spin operator of NV A(B). Electron spin flip-flop terms such as $(S_{iA} S_{iB})$ can be neglected as long as the energetic detuning between two spins is larger than their dipolar coupling $\nu_{\text{dip}}$ (see Supplementary Information). The two defects are oriented along two different directions of the diamond lattice and hence the orientation dependence of the fine structure term allows for individual addressing by different microwave frequencies. To investigate the magnetic dipolar coupling between the two defects we induce spin transitions ($\Delta m_S = \pm 1$) on both defects and use NV A as a sensitive magnetometer\textsuperscript{22} to measure spinflip-induced changes of the magnetic dipole field of NV B yielding a dipolar coupling constant of $\nu_{\text{dip}} = 4.93 \pm 0.05$ kHz (Fig. 1e). The effective coupling strength can be enlarged up to four...
times by exploiting the qutrit nature of the triplet spin in each NV centre. Namely, the quantum phase of a superposition state with Δmoplast = ±2 evolves twice as fast in a given magnetic fields as the Δmoplast = ±1 superposition. Furthermore, a spinflip by Δmoplast = ±2 induces a twice as strong magnetic field change compared with the case of Δmoplast = ±1. Hence, using Δmoplast = ±2 (double quantum transitions, DQ) on both NVs yields νDQ = 19.7 ± 0.2 kHz. It is worth mentioning that these double quantum coherences have half the dephasing time of a single quantum transition under the influence of Markovian magnetic field noise. To create high-fidelity entanglement, strong coupling has to apply (that is, νDQ > 1/T2, where T2 is the relevant coherence time). The present moderate coupling is masked by spectral diffusion of the two individual electron spins (T2DQ = 27.8 ± 0.6 μs and T2DQ = 22.6 ± 2.3 μs); that is, νDQ < 1/T2. This limitation can be overcome by eliminating low-frequency environmental noise components through further refocussing steps in the entanglement process resulting in a new lower limit for strong coupling νDQ > 1/T2. The electron spin relaxation and coherence times of the two NVs are T1 = 1.12 ± 0.26 ms, T2ADQ = 150 ± 18 μs and T2BDQ = 514 ± 50 μs. The measured values for dipolar interaction and T2DQ allow a maximum distance of 29.6 ± 1.4 nm between the two defects. The actual distance obtained by involving microwave-assisted super-resolution microscopy yields 25 ± 2 nm. Note that the coupling did not change over months, indicating the room-temperature stability of the defect pair.

After optically initializing the system in |mSA, mSB⟩ = |00⟩ a double quantum π/2 rotation on both NVs leads to 1/2(|−1⟩−|−1⟩ − |−1⟩ − |1⟩ + |11⟩). Under the influence of mutual dipolar coupling the system is evolving freely for a time τ resulting in a state-dependent phase acquisition 1/2(e−iΔφ|−1⟩−|−1⟩ − |−1⟩ − |1⟩ + |11⟩) where φ = 2πνDQτ and τ is the correlated phase due to dipolar interaction. After a double quantum π rotation and a further free evolution period τ, a second phase is accumulated 1/2(e−iΔφ|−1⟩−|−1⟩ − |−1⟩ − |1⟩ + |11⟩) with a final double quantum π/2 rotation the accumulated phase is mapped onto 1/2(|−1⟩−|−1⟩ + |−1⟩ + |1⟩ + |11⟩). For |τ = 1/2νDQ = 25 μs this is φDQ = (1/√2)(|−1⟩−|−1⟩ + |1⟩ + |11⟩) a maximally entangled Bell state (for details see Supplementary Information). Using local operations this state can be transformed into a set of different entangled states, for example two π pulses transform to ΦDQ to Φ− = (1/√2)(|00⟩ − i|11⟩). Figure 2b shows the state evolution on application of the entanglement gate as a function of interaction time τ. The blue line is a simulation of the entangling gate using Hamiltonian (1) with coherence times taken from experimental data. For |τ = 12.5 μs the state has evolved to ΦDQ. As the evolution into ΦDQ would not be visible in the fluorescence signal it was transformed into Φ− using local gates. We have performed a density matrix tomography of the final entangled state (for details see Supplementary Information). The fidelity of the reconstructed density matrix with respect to the target state |Φ−⟩ = 0.67 ± 0.04, which is below the simulated fidelity of 0.89. (Fidelity is defined as the proximity of two states given by F = Tr(ρσ), where σ is the measured quantum state and ρ is the target state.) The main reason for this discrepancy is due to errors resulting from the finite duration of microwave pulses. In addition, we quantify the entanglement according to ref. 23 by using the von Neumann relative entropy as
Fig. 2 | Bell state tomography. a, Quantum circuit diagram of the entanglement scheme. A spin echo sequence on both individual spins reduces the effect of local noise while preserving the spin-spin interaction. The latter realizes a controlled phase gate that finally leads to the Bell state $\Phi^{+}_{00}$ after an evolution time of $1/\Delta_{\text{hh}}$. b, Final state of the entanglement scheme as a function of evolution times $\tau$. The graph includes the simulated fidelity of reaching $\Phi^{-}$. Note that $\Phi^{+}_{00}$ was transformed to $\Phi^{-}$ at the end of the sequence to allow for a fluorescence contrast. c, d, Real and imaginary part of the density matrix tomography of the $\Phi^{+}_{00} = (1/\sqrt{2})(|00\rangle + |11\rangle)$ state.

Fig. 3 | Two-photon correlation measurements. a, Results of two-photon correlation measurement for entangled and mixed states. Photons close to the zero delay have been discarded. The inset shows the fitted amplitude of two-photon coincidences at $\tau = 20$ ns. b, Reconstructed population correlation of a $\Phi^{-} = (1/\sqrt{2})(|00\rangle - |11\rangle)$ state in a reduced basis of $m_0 = 0$ and $m_3 = -1$. The fidelity of the main diagonal is $F(\Phi^{\text{class}}) = 1.07 \pm 0.19$. c, For $\Psi^{-} = (1/\sqrt{2})(|01\rangle - i|10\rangle)$ the main diagonal fidelity is $F(\Psi^{\text{class}}) = 0.81 \pm 0.15$ (see Supplementary Information for details). The error bars are given by the fitting error of the photon correlation signal.

$$E(\sigma^{\text{class}} \parallel \rho) = \min_{\rho_{\text{diem}}} \text{tr}(\sigma \ln(\sigma / \rho)) \approx 0.16 \ (0 \ \text{for no entanglement}, \ln 2 \approx 0.69 \ \text{for a maximal entangled state}).$$

Entanglement between spins is also inferred from fluorescence emission properties of the entangled defect pair. The steady-state fluorescence emission of $\Psi^{-} = (1/\sqrt{2})(|01\rangle - i|10\rangle)$, $\Phi^{-} = (1/\sqrt{2})(|00\rangle - |11\rangle)$ as well as a correspondingly separable spin state of both NV centres (for example $(1/2)(|00\rangle + |10\rangle + |01\rangle + |11\rangle)$) is identical. However, two-photon correlations reveal a difference between spin-entangled and mixed states. A $\Psi$ state has a higher probability of simultaneously emitting two photons than an uncorrelated superposition state whereas a $\Psi$ state has a lower probability. In Fig. 3, two-photon correlation measurements and the corresponding classical correlations are shown.

The lifetime of the entangled states is limited by electron spin dephasing measured to be $T_{\chi, \text{DO}} = 27.8 \pm 0.6 \mu s$ and $T_{\Omega, \text{DO}} = 22.6 \pm 2.3 \mu s$. The measured entanglement lifetime is $T(\Phi^{+}_{00}) = 28.2 \pm 2.2 \mu s$ and $T(\Psi^{+}_{00}) = 23.7 \pm 1.7 \mu s$ (Fig. 4c and Supplementary Information). It is interesting to note that the lifetimes for states $\Phi^{+}$ and $\Psi^{+}$ are identical although $\Psi^{+}$ is known to constitute a decoherence-free subspace for dephasing processes that are dominated by magnetic field noise. However, cancellation of decoherence effects in $\Psi^{+}$ occurs only if the magnetic field field is identical for both NV A and NV B (that is non-local). Apparently this is not the case for the pair. One reason is the different orientation of the pair of NVs with respect to $B_{\text{hh}}$, which would result in non-ideal decoherence-free subspaces. In addition, from a previous analysis of spin dephasing in diamond defect centres it became clear that electron spin dephasing is dominated by nuclear spins in the nanometre vicinity of the defect.

To store entanglement for a longer period, we designed an experimental scheme (Fig. 4a) to transfer electron spin entanglement to $^{15}$N nuclear spins of the NV. Instead of swapping entanglement by driving nuclear spins directly, we used a combination of a non-aligned static magnetic field previously introduced for state storage and selective gates on the electron spins to generate electron nuclear SWAP gates on both NVs. The entanglement swapping protocol used can potentially reach
Entanglement storage in $^{15}$N. a, Entanglement storage scheme. Selective π pulses creating a SWAP operation store the entanglement in the nitrogen nuclear spin. b, Fast Fourier transform of the entangled states’ collective phase evolution after entanglement storage (orange) and a reference measurement without entanglement storage (blue). c, The dependence of the entanglement recovery efficiency on the storage time is shown in orange. The solid orange line is the exponential fit to the data whereas the orange dashed line is the simulated storage and retrieval efficiency given the imperfect SWAP gate. Magenta dots and lines are the measurement and fit of $T_1$. The blue and green lines are entanglement lifetimes without storage. The error bars are given by the fitting error of the fast Fourier transform peak.

Methods

NV defects are formed either by nitrogen incorporation during growth or by implantation of nitrogen into high-purity diamond material with a subsequent annealing step. Here we have chosen the latter method to generate proximal diamond defect pairs. The pair was produced by ion implantation in isotope-enriched $^{12}$C diamond (99.99%) using a specially designed micro mask with high-aspect-ratio apertures (1:100). Ground-state depletion imaging was performed to identify suitable candidates, which were investigated with double electron–electron resonance. The sample was investigated in a home-built confocal microscope. For coherent control, microwave radiation was synthesized (Rhode-Schwarz SMQ 03B) and modulated by an IQ (in-phase and quadrature) mixer with an arbitrary waveform generator (Tektronix AWG 520). The microwaves were applied by means of a microstructure forming a split ring resonator lithographically fabricated on the diamond surface.

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Author contributions
F.D., I.J. and B.N. carried out the experiments. S.P., C.T. and J.M. prepared implantation masks and samples. P.N., F.J. and J.W. supervised experiments. N.Z. analysed experimental data. F.D., P.N., I.J. and J.W. wrote the paper.

Additional information
Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to J.W.

Competing financial interests
The authors declare no competing financial interests.