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SUPPLEMENTARY INFORMATION
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# Electron spin coherence exceeding seconds in high-purity silicon

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**1. Instantaneous diffusion in case of uniform distribution of donors in silicon.**

Instantaneous diffusion is a decoherence process directly associated with applied microwave pulses.[1-3] In a two-pulse echo experiment, $(90° - \tau - 180° - \tau - \text{echo})$, when the second (refocusing) pulse flips two dipole-coupled spins *simultaneously* the dipole interaction does not change its sign and therefore it does not refocus. The unrefocused dipole interactions lead to dephasing (decoherence) of spins in pairs, the effect termed instantaneous diffusion. In case of a selected spin pair with a defined dipole interaction, *D*, instantaneous diffusion leads to an oscillating echo signal, $V(\tau) \sim \cos(D\tau)$. In ensemble measurements and assuming spins are uniformly distributed, random spin pairs can form with a broad range of *D* interactions and therefore the echo oscillations occur at random frequencies. After ensemble averaging, the oscillations wash out leaving an overall exponential echo decay:

$$V(\tau) \sim \exp(-2\tau/T_2),$$

where $\frac{1}{T_2} = \frac{5}{2} \cdot \frac{\mu_0}{4\pi} \cdot \frac{(g\beta_e)^2}{\hbar} \cdot \frac{[P]}{2}$, with $\mu_0$ vacuum permeability, $g$ electron g-factor, $\beta_e$ Bohr magneton, $\hbar$ Plank constant, and $[P]$ donor density. Thus, $\frac{1}{T_2}$ changes proportionally with [P].

The instantaneous diffusion can be suppressed by using a two-pulse experiment, $(90° - \tau - \theta_2 - \tau - \text{echo})$, with the second pulse being set to a small rotation angle, $\theta_2$. In that case, the effect of instantaneous diffusion scales down proportionally with $\sin^2(\theta_2/2)$ and the observed decay rate is $\frac{1}{T_2} = \frac{5}{2} \cdot \frac{\mu_0}{4\pi} \cdot \frac{(g\beta_e)^2}{\hbar} \cdot \frac{[P]}{2} \sin^2(\theta_2/2)$.

**2. Spin decoherence by spectral diffusion due to $T_1$-induced spin flips of neighbor donors at intermediate temperatures 4-8 K.**

Spin flips of neighbor donors caused by $T_1$ relaxation processes are seen by the central spin as random dipolar field fluctuations (Figure 3d in the main text). These field fluctuations

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lead to decoherence of the central spin, a process termed $T_1$-type spectral diffusion. In a two-pulse echo experiment, $(90° - \tau - 180° - \tau - \text{echo})$, this spectral diffusion process results in a non-exponential echo signal decay.[4,5] In the limit of $T_1 >> \tau$ (inter-pulse delay), the decay follows a quadratic exponential dependence:

$$V(\tau) \sim \exp[-(2\tau/T_{SD})^2], \qquad (1)$$

with characteristic spectral diffusion time $T_{SD}^2 = \frac{18\sqrt{3}}{\mu_0} \cdot \frac{\hbar}{(g\beta_e)^2} \cdot \frac{T_1}{[P]}$.

Figure A1 shows the two-pulse echo decays measured for a $^{28}Si$ crystal with donor density $1.2 \cdot 10^{14}/cm^3$ at three different temperatures. The small rotation angle $\theta_2$ = 22 deg was used to suppress the otherwise dominant instantaneous diffusion effects. The solid lines are theoretically predicted decays according to Eq. (1). We note that there are no fit parameters and the decay were calculated using the known donor density in the sample and the measured $T_1$ times at each temperature. The simulated decays correlate closely with the experimental curves at 4.7 and 5.8 K, revealing that $T_1$-type spectral diffusion is the dominant decoherence process at these two temperatures. On the other hand, the predicted decay is much slower than seen in the experiment at 2.1 K. The $T_1$-type spectral diffusion makes a negligible contribution at this low temperature, and some other processes dominate the relaxation. It is shown in the main text that this other process is spectral diffusion due to spin flip-flops in neighbor donor pairs.

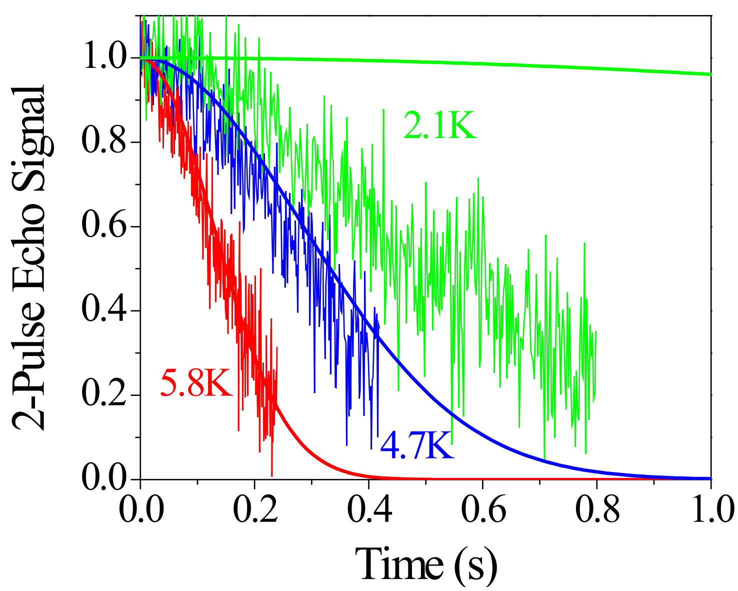


Figure A1. Experimental and simulated two-pulse echo decays of phosphorus donors in $^{28}Si$ doped with $1.2 \cdot 10^{14}$ donors/cm$^3$ at three temperatures as indicated. The experimental decays were measured with a pulse sequence $(90° - \tau - 180° - \tau - \text{echo})$ using a small rotation angle $\theta_2$ = 22 deg to suppress instantaneous diffusion. The simulated decays were calculated using Eq.(1) and assuming $T_1$ = 1.6 s (5.8 K), 8 s (4.7 K), and 1300 s (2.1 K) as measured in separate experiments.

**3. Scaling of "intrinsic" $T_2$ versus donor density at low temperatures.**

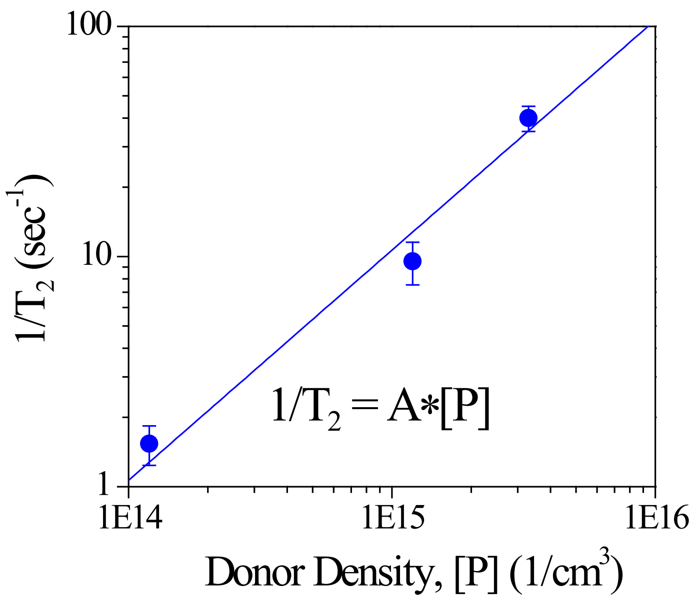


Figure A2. "Intrinsic" $T_2$ obtained after suppressing instantaneous diffusion plotted as a function of donor density in $^{28}$Si crystals. Measurement temperatures ~ 2 K. The nearly linear dependence is consistent with spectral diffusion due to donor flip-flops as predicted by the recent theory in Ref. [6].

**4. Intrinsic distribution of resonance offsets ($\Delta\nu = \nu_1 - \nu_2$) between donors in pairs in a $^{28}$Si crystal without an external field gradient.**

In the main text (Figure 4a) we showed that application of an external field gradient suppresses flip-flops in donor pairs leading to longer donor $T_2$. For the gradient of 10 μT/mm applied to a $^{28}$Si crystal with $1.2\cdot10^{14}$ donors/cm$^3$ we estimated the flip-flop suppression factor to be $S_{ff} = 13\%$.

Flip-flops in donor pairs are driven by dipolar interactions and also controlled by local inhomogeneous fields. For a flip-flop to occur requires that the dipolar interaction ($a_{dd}$) within a pair be greater than the inhomogeneous offset of resonant frequencies ($\Delta\nu = \nu_1 - \nu_2$) of two spins involved. Thus, a pair can flip-flop only if $a_{dd} > \Delta\nu$, and the pair cannot flip-flop if $a_{dd} < \Delta\nu$. By applying a known external field gradient one can controllably increase $\Delta\nu$, to make it greater than $a_{dd}$, and thus to switch off flip-flops in those pairs that were flip-flopping before applying the gradient.

For donor density of $1.2\cdot10^{14}$ donors/cm$^3$ the average distance between donors with opposite spins (ones that can flip-flop) is 255 nm giving an average dipolar interaction of $a_{dd}$ ~ 2 Hz. Donor resonance offsets ($\Delta\nu$) in a $^{28}$Si crystal are described by an unknown distribution that

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arises from various inhomogeneous fields, including hyperfine fields from random configurations of $^{29}Si$ nuclei, local crystal strains from various impurities and defects, etc. The shape of this distribution is predicted to be Lorentzian[7] and the width of the distribution is unknown. The question then arises whether we can estimate the width using the flip-flop suppression factor, $S_{ff}$ = 13%, as determined for the 10 μT/mm gradient.

Figure A3 shows the simulated Δν distributions. We assume a Lorentzian inhomogeneous linewidth of Δν ~ 15 Hz in the absence of a gradient (red trace). The 10 μT/mm gradient was applied orientated at 45 degrees with respect to the external magnetic field, $B_0$, as it was in the experiment, and then the offset distribution was calculated for the average donor-donor distance of 255 nm (corresponding to $1.2{\cdot}10^{14}$ donors/cm$^3$). It is seen that the offset distribution transforms significantly upon applying the gradient (blue trace). In both cases the average $a_{dd}$ ~ 2 Hz (at $1.2{\cdot}10^{14}$ donors/cm$^3$) is smaller than the width of the distribution. Only pairs with resonant offsets less than 2 Hz can flip-flop, which are the pairs to the left of green dashed line in Figure A3. Thus, the integrated number of flip-flopping pairs changes from 5% in the absence of a gradient to 0.7% in the presence of a 10 μT/mm gradient. Their ratio corresponds to a flip-flop suppression factor of 14% which is close to that found in the experiment.

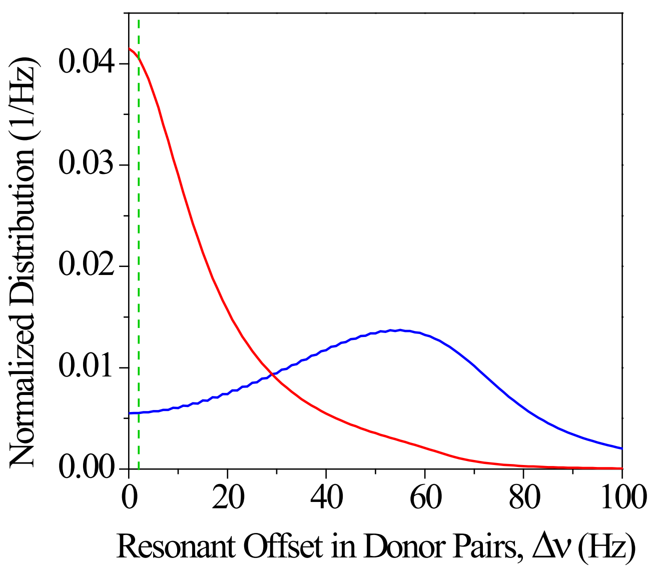


Figure A3. Distribution of resonance offsets ($\Delta\nu = \nu_1 - \nu_2$) between donors in pairs at concentration $1.2{\cdot}10^{14}$ donors/cm$^3$, in the absence (red) and presence (blue) of the externally applied field gradient of 10 μT/mm. The gradient is assumed to be oriented at 45 degree with respect to the external magnetic field, $B_0$. Dashed vertical line (green) indicates the average dipolar interaction $a_{dd}$ ~ 2 Hz (at $1.2{\cdot}10^{14}$ donors/cm$^3$). Only donor pairs to the left of this line have their Δν smaller than $a_{dd}$ and therefore can flip-flop.

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