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Reaching the quantum limit of sensitivity in electron spin resonance

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The detection and characterization of paramagnetic species by electron spin resonance (ESR) spectroscopy is widely used throughout chemistry, biology and materials science, from in vivo imaging to distance measurements in spin-labelled proteins. ESR relies on the inductive detection of microwave signals emitted by the spins into a coupled microwave resonator during their Larmor precession. However, such signals can be very small, prohibiting the application of ESR at the nanoscale (for example, at the single-cell level or on individual nanoparticles). Here, using a Josephson parametric microwave amplifier combined with high-quality-factor superconducting microwave resonators cooled at millikelvin temperatures, we improve the state-of-the-art sensitivity of inductive ESR detection by nearly four orders of magnitude. We demonstrate the detection of 1,700 bismuth donor spins in silicon within a single Hahn echo with unit signal-to-noise ratio, reduced to 150 spins by averaging a single Carr–Purcell–Meiboom–Gill sequence. This unprecedented sensitivity reaches the limit set by quantum fluctuations of the electromagnetic field instead of thermal or technical noise, which constitutes a novel regime for magnetic resonance. The detection volume of our resonator is ~0.02 nl, and our approach can be readily scaled down further to improve sensitivity, providing a new versatile toolbox for ESR at the nanoscale.

A wide variety of techniques are being actively explored to push the limits of the sensitivity of electron spin resonance (ESR) to the nanoscale, including approaches based on optical9,10 or electrical10,11 detection, as well as scanning probe methods12,13. Our focus in this work is to maximize the sensitivity of inductively detected pulsed ESR to maintain the broad applicability to different spin species as well as fast high-bandwidth detection. Pulsed ESR spectroscopy proceeds by probing a sample coupled to a microwave resonator of frequency ω0 and quality factor Q with sequences of microwave pulses that perform successive spin rotations, triggering the emission of a microwave signal called a spin-echo whose amplitude and phase contain the desired information about the number and properties of paramagnetic species. The spectrometer sensitivity is conveniently quantified by the minimal number of spins Nmin that can be detected within a single echo6. Conventional ESR spectrometers use three-dimensional resonators with moderate quality factors in which the spins are only weakly coupled to the microwave photons and thus obtain a sensitivity of Nmin ~ 1 × 1015 spins at T = 300 K and X-band frequencies (ω0/2π ~ 9–10 GHz). To increase the sensitivity, micro-fabricated metallic planar resonators with smaller mode volumes have been used, resulting in larger spin–microwave coupling. Combined with operation at T = 4 K and the use of low-noise cryogenic amplifiers and superconducting high-Q thin-film resonators, sensitivities up to Nmin ~ 1 × 107 spins have been reported, which represents the current state of the art.

Further improvements in the sensitivity of ESR spectroscopy can be obtained by cooling the sample and resonator down to millikelvin temperatures that satisfy T ≪ ℏω0/kB at X-band frequencies. As a result, both the spins and the microwave field reach their quantum ground state, which is the optimal situation for magnetic resonance because the spins are then fully polarized and thermal noise is suppressed. The noise in the emitted echo signal is essentially due to vacuum quantum fluctuations of the microwave field, with a dimensionless spectral power density of nΩ = S(ω)/ℏω = 1/2, possibly supplemented by extra noise nΩ due to the spontaneous emission of the spins (Supplementary Section IV). However, the total noise spectral density in the detected signal n = nΩ + nΩ + namp also includes the added noise namp of the first amplifier of the detection chain. Benefiting from the low noise afforded by low-temperature operation thus requires nearly noiseless amplifiers at microwave frequencies, as were recently developed in the context of superconducting quantum circuits. These Josephson parametric amplifiers (JPAs) are operated at millikelvin temperatures, have a bandwidth of up to ~100 MHz, and a low saturation input power (typically 1–10 fW)17,18. They have been shown to add the minimum amount of noise permitted by quantum mechanics19: namp = 0.5 when both field quadratures are equally amplified (non-degenerate mode)20 and namp = 0 when only one quadrature is amplified (degenerate mode)20. JPAs have been used so far for reading out the state of superconducting qubits, the motion of nanomechanical oscillators and the charge state of a quantum dot, as well as for high-sensitivity magnetometry. Here, we show that they are also well suited to amplifying the weak and narrowband signals emitted by small numbers of spins, with the ultimate sensitivity allowed by quantum mechanics, enabling us to demonstrate a four orders of magnitude improvement in sensitivity over the state of the art.

We use an ensemble of Bi donors implanted over a 150 nm depth into an isotopically enriched 28Si crystal, on top of which is patterned a superconducting Al thin-film resonator consisting of an interdigitated capacitor in parallel with a wire inductance (see Fig. 1 for a sketch of the set-up). Due to this geometry, the microwave field B0 cos ω0t couples only to the NBi ~ 4 × 107 implanted Bi atoms located in the area below the wire. The
The Al microwave resonator with frequency \( \omega_0 \) consists of an interdigitated capacitor in parallel with a 5-μm-wide wire inductor, fabricated on a Bi-doped 28Si epi-layer. The sample is mounted in a Cu box, thermally anchored at 12 mK, and probed by microwave pulses via asymmetric antennas coupled to the resonator with rates \( k_1 = 1.2 \times 10^7 \text{s}^{-1} \) and \( k_2 = 5.6 \times 10^7 \text{s}^{-1} \). A magnetic field \( B_0 \) is applied parallel to the resonator inductance. Microwave pulses at \( \omega_0 \) are sent by antenna 1, and the microwave signal leaving via antenna 2 is directed to the input of a JPA. The JPA is powered by a pump signal at \( \omega_0 \approx 2\omega_0 \), and its output is further amplified at 4 K by a HEMT amplifier, followed by amplification and demodulation at room temperature, yielding the two field quadratures \( I(t), Q(t) \). Energy levels of Bi donors in Si, expressed in units of frequency (see spin Hamiltonian in Supplementary Section II). 

In the low-field regime, the 20-electro-nuclear energy states are best described by their total angular momentum \( F = S + I \) and its projection \( m_F \); they can be grouped in an \( F = 4 \) ground and an \( F = 5 \) excited multiplet separated by a frequency of \( 5A/h = 7.38 \text{GHz} \) in zero field (Fig. 1). With the chosen orientation of \( B_0 \), the Bi microwave field generated by the resonator is perpendicular to the spin quantization axis and only transitions obeying \( |\Delta m_F| = 1 \) have a significant matrix element (Fig. 1d) for \( B_0 \leq 10 \text{mT} \). Their frequency in the ~7.3–7.5 GHz range makes Bi:Si an ideal system for coupling to superconducting Al resonators, which can only withstand fields below ~10 mT.

Figure 1 | Experimental set-up and spin system. a. The Al microwave resonator with frequency \( \omega_0 \) consists of an interdigitated capacitor in parallel with a 5-μm-wide wire inductor, fabricated on a Bi-doped 28Si epi-layer. The sample is mounted in a Cu box, thermally anchored at 12 mK, and probed by microwave pulses via asymmetric antennas coupled to the resonator with rates \( k_1 = 1.2 \times 10^7 \text{s}^{-1} \) and \( k_2 = 5.6 \times 10^7 \text{s}^{-1} \). A magnetic field \( B_0 \) is applied parallel to the resonator inductance. Microwave pulses at \( \omega_0 \) are sent by antenna 1, and the microwave signal leaving via antenna 2 is directed to the input of a JPA. The JPA is powered by a pump signal at \( \omega_0 \approx 2\omega_0 \), and its output is further amplified at 4 K by a HEMT amplifier, followed by amplification and demodulation at room temperature, yielding the two field quadratures \( I(t), Q(t) \). Energy levels of Bi donors in Si, expressed in units of frequency (see spin Hamiltonian in Supplementary Section II). 

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In our case, the \( |F,m_F\rangle = |4, -4\rangle \rightarrow |5, -5\rangle \) and \( |4, -3\rangle \rightarrow |5, -4\rangle \) transitions are expected to be resonant with \( \omega_0 \) at \( B_0 = 5 \) and 7 mT, respectively, corresponding peaks in the integrated spin-echo signal (of duration \( T_2 = 20 \mu \text{s} \)) are indeed measured as shown in Fig. 2a–c. Each transition consists of two sub-peaks, with an inhomogeneous linewidth \( \Gamma/2\pi = 2 \text{MHz} \) at 4 K. The spectrometer sensitivity is estimated by measuring the integrated spin-echo signal (Fig. 2b), with a 100 kHz Rabi frequency for a remarkably low input power of 3 pW (ref. 4). The decay of the integrated echo signal as a function of the total delay \( \tau \) between the initial \( \pi/2 \) pulse and the echo is well fitted by an exponential decay with a time constant \( T_2 = 10 \mu \text{s} \), a typical coherence time for Bi:Si (ref. 28; Fig. 2d). Given the high quality factor of the resonator, the \( \pi/2 \) pulse has an exponential tail with a characteristic time \( \tau = 2\mu \tau = 14 \mu \text{s} \), so the minimum \( T_2 \) that one could measure in this set-up is ~50 μs. The energy relaxation time \( T_1 \) is measured by the inversion recovery method to be \( T_1 = 0.3 \mu \text{s} \) (Fig. 2e), allowing us to use a 1 Hz repetition rate throughout this work.

The spectrometer sensitivity is estimated by measuring the signal-to-noise ratio (SNR) of a single echo. The JPA is operated in the degenerate mode, with the phase of the pump signal chosen such that the echo signal is entirely on the amplified quadrature. With these optimal settings, the amplitude SNR of the echo shown in Fig. 3a is found to be \( 7 \pm 1 \), one order of magnitude larger than the SNR obtained under the same conditions but with the JPA pump turned off so that it simply reflects the echo signal. This improvement is consistent with a noise reduction from \( n \approx 50 \)
Figure 2 | Sample characterization. a, Hahn-echo sequence (top), triggering the emission of an echo (bottom). Plotted are the demodulated quadratures $I(t)$ (green squares) and $Q(t)$ (red diamonds), as well as the echo amplitude $A(t) = \sqrt{I(t)^2 + Q(t)^2}$ (blue circles), from which the echo quadrature area $X_e = \int_{0}^{\infty} I(t)Q(t)dt$ (with $X = I,Q$) and amplitude area $A_e = \int_{0}^{\infty} A(t)dt$ are extracted. The data are taken for $B_0 = 5.2$ mT. b, Normalized amplitude echo area as a function of refocusing pulse amplitude $A_e$ (rescaled by the amplitude needed for a $\pi$ pulse) showing Rabi oscillations. Blue circles are data points and red curve is an exponentially damped cosine fit. c, Amplitude echo area (blue circles joined by dashed lines) as a function of magnetic field $B_0$, showing two principal resonances, each split into a doublet due to the effect of strain on the donors below and next to the Al wire inductor. d, As the total time 2$t$ between the initial $\pi/2$ pulse and the echo is increased, the recovered $Q$ quadrature echo area decays with an exponential behaviour (red curve is a fit), yielding a spin coherence time of $T_2 = 8.9$ ms. e, The inversion recovery sequence (see inset) is used to measure the spin relaxation time $T_1 = 0.35$ s. Red curve is an exponential fit to the experimental data (blue circles).

(with the JPA off) to $n \approx 0.5$, thus close to the quantum limit, and with calibration measurements performed on the JPA itself (Supplementary Section III).

Of all the neutral Bi donors within the resonator mode volume, only those whose frequency lies within the resonator linewidth $\kappa = \omega_0/Q$ and that are in the $|4, -4\rangle$ state contribute to the echo signal. A rough estimate of the number of spins is therefore obtained as $N_{\text{min}}(\kappa) = 4 \times 10^4$, an overestimate given that only a fraction of implanted atoms show a magnetic resonance signal due to either crystal damage or to donor ionization. For a more accurate
determination, the time-dependent absorption of a microwave pulse at $\omega_0$ recorded and fitted to a simple model (Fig. 3b) and Supplementary Section IV) allows us to obtain an absolute calibration of the spin density. A whole spin-echo sequence is then measured and simulated (Fig. 3c). The quantitative agreement with the observed echo amplitude establishes (from the simulations) that $1.2 \times 10^4$ spins are excited during the sequence. This implies a $\sim 30\%$ yield between number of implanted atoms and neutral donors, compatible with previous reports.

Overall, the spectrometer can therefore detect down to $N_{\text{min}} = 1.2 \times 10^4/7 = 1.7 \times 10^3$ spins with an SNR of unity in a single Hahn echo, and has a corresponding sensitivity of $1.7 \times 10^3$ spins/Hz$^{1/2}$ given the 1 Hz repetition rate. This four orders of magnitude improvement over the state of the art is in qualitative agreement with the prediction of a simplified model (Supplementary Section IV) $N_{\text{min}}(\kappa) \approx \sqrt{\pi g/\kappa T_2}$ (1/g), where $g$ is the coupling constant of a single spin to the resonator microwave field, estimated for our geometry to be $g/2\pi = 55$ Hz, which yields $N_{\text{min}} = 400$ spins. The sensitivity can be further improved with a Carr–Purcell–Meiboom–Gill pulse sequence, adding $m \pi$ pulses after the first echo in order to recover $m$ echoes instead of a single one, yielding an increase in SNR of $-m^{1/2}$ (ref. 7). The applicability of this technique depends on factors such as the spin coherence time $T_2$ of the sample and the echo duration $T_{\text{E}}$. For our $^{28}\text{Si:Bi}$ sample,
up to 600 echoes are obtained, as shown in Fig. 4, with a corresponding tenfold increase in the SNR and an unprecedented sensitivity of 150 spins in a single shot, or 150 spins/Hz$^{1/2}$.

A wide range of species, including molecular magnets, Gd spin-labels and high-spin defects in solids, can be studied by ESR spectroscopy on nanoscale samples such as single cells, small molecular ensembles, nanoparticles and nanodevices. We predict that a further two orders of magnitude sensitivity enhancement is possible by reducing the resonator transverse dimensions down to the nanometre scale, which would then be sufficient for detecting individual electron spins.

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**Author contributions**


**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 P.B.

**Competing financial interests**

The authors declare no competing financial interests.