Nuclear spin defects are archetypal models of qubits in solid state systems. We expect them to have long coherence times and to be well controlled [1,2]. However, to date they have mainly been studied via their interaction to a neighboring electron spin [1–4]. Such experiments are indirect probes of the local fields seen by the nuclear spins. Here, we directly observe nuclear spin defects in a dilute sample of silicon, and through a combination of free induction decay (FID) and echo measurements we characterize the local field and its fluctuations.

The phosphorus donor impurity in silicon is a potentially promising candidate for a hybrid quantum information processor [5]. In natural abundance bulk silicon, the 300–600 μs coherence time of the donor electron spin at low temperatures has been shown to be limited primarily by spectral diffusion due to the 29Si nuclei (4.7% natural abundance) [6]. Similar coherence times have also been measured at the level of individual donors [3,4]. In the bulk, this coherence time has been extended to 0.6 s by isotopically engineering the silicon lattice to reduce the 29Si nuclear spin concentration and simultaneously reduce the donor concentration to minimize the dipolar coupling between electron spin donors (thus reducing instantaneous diffusion effects) [7]. The 31P donor nuclear spin has also been shown to have extremely long coherence times (180 s at low temperature and B = 845 G) [8], limited primarily by electron spin fluctuations. By ionizing the donors with below-gap narrow-line laser excitation and using dynamical decoupling techniques, the phosphorus nuclear spin coherence times were extended to 39 min at room temperature and 3 h at 4.2 K in a silicon-28 lattice, at ~845 G [9]. It has recently been shown that it is possible to optically hyperpolarize the 31P donor nuclear spins in silicon at relatively low doping concentrations (~1015 cm−3) in two different regimes. At high magnetic field (~8.5 T), the phosphorus nuclear spins were detected by using both electron spin resonance (ESR) and electrically detected magnetic resonance (EDMR) [10–13] under white light illumination. The optical nuclear hyperpolarization of ~68% built up over a characteristic time of 120 s [12].
Because of the limited penetration of the light into the silicon, the hyperpolarization occurred primarily near the illuminated surface. At low magnetic fields, the nuclear spin polarization (86%) was measured by using photoluminescence excitation spectroscopy with both resonant and above-band-gap laser excitation [8,14,15] and showed subsecond optical hyperpolarization time scales.

Here we demonstrate the direct inductive readout of the phosphorus nuclear magnetic resonance (NMR) signal at a phosphorus donor concentration of \( \sim 10^{15} \text{ cm}^{-3} \) [16], following hyperpolarization of bulk \( ^{31}\text{P} \) nuclei using nonresonant infrared laser excitation, at high field and low temperature. Previous direct NMR measurements of phosphorus nuclear spins in silicon have been possible only at very high doping concentrations (\( \sim 10^{18} \text{ cm}^{-3} \)) [17,18], about 3 orders of magnitude higher than the concentrations used in this Letter. This inductive readout of the phosphorus donor nuclei allows us to measure nuclear spin properties in the bulk of the sample.

We used a simple NMR detection setup where a cylindrical \( ^{28}\text{Si} \)-enriched crystal [19] with a phosphorus concentration of \( 1.5 \times 10^{15} \text{ cm}^{-3} \) (boron concentration \( \sim 1.0 \times 10^{14} \text{ cm}^{-3} \), dislocation-free crystal) was placed in a rhodium-flashed, silver-plated copper, rf coil, wired to a low temperature LC circuit. All experiments presented here were performed at temperatures 4.2 or 1.7 K \( \pm 0.3 \text{ K} \), and the magnetic field was 6.71 T. The buildup of the high \( ^{31}\text{P} \)-spin polarization was accomplished by illuminating the sample with a 100 mW, 1047 nm, above-band-gap laser, with a linearly polarized beam of 8 mm effective size (see Supplemental Material [20]). The (indirect) band gap in silicon is 1.12 eV which corresponds to an optical wavelength of 1100 nm. The penetration depth for 1047 nm light in silicon at cryogenic temperatures is a few centimeters which allowed the excitation of bulk phosphorus impurities [27].

The effective Hamiltonian of the phosphorus donor impurity at high magnetic field is

\[
\mathcal{H} = -\gamma_n B_z I_z - \gamma_e B_z S_z + \frac{2\pi}{\hbar} A S_z I_z.
\]

where \( \gamma_n/2\pi = 17.23 \text{ MHz/T} \) and \( \gamma_e/2\pi = -28.024 \text{ GHz/T} \) are the nuclear and electron gyromagnetic ratios, respectively, and \( A = 117.54 \text{ MHz} \) is the isotropic hyperfine interaction term. In the high-field limit, the eigenstates are almost exactly given by the product states \( |\uparrow_n \uparrow_n\rangle, |\downarrow_n \downarrow_n\rangle, |\uparrow_e \downarrow_n\rangle, |\downarrow_e \uparrow_n\rangle \) [28]; see Fig. 1(b). At 6.71 T, the thermal electron spin polarization is 79% at 4.2 K and 99% at 1.7 K, while the thermal nuclear spin polarization is 0.07% at 4.2 K and 0.16% at 1.7 K. We probed the nuclear spins in the lower spin electron manifold, transition \( \nu_{n_1} = 174.08 \text{ MHz} \) [see Fig. 1(b)].

Figure 1(c) illustrates the experimental sequence used to measure the buildup of the hyperpolarization. Following a saturation train of \( \pi/2 \) pulses to destroy the remnants of the hyperpolarization from the previous experiment, the nuclear spins are polarized with laser irradiation. The NMR signal was measured by using a single \( \pi/2 \) rf pulse (duration 8.5 \( \mu \text{s} \)), and the resulting free induction decay was Fourier transformed to produce the NMR spectrum. A typical signal is show in Fig. 1(d), produced with 200 s laser irradiation. The full line width at half maximum (FWHM) is \( \sim 160 \text{ Hz} \) (consistent with \( T_2^* \sim 2 \text{ ms} \)).

The buildup of the hyperpolarization was measured by varying the laser excitation time (or polarization time), from 2 s to 10 h (Fig. 2). This buildup was measured at both 4.2 and 1.7 K. The ratio of the steady state signals at these temperatures was measured to be 5.88. We were able to fit the buildup curve at 4.2 K by using a single exponential fit with a characteristic time of 577 s. The measured buildup at 1.7 K showed biexponential behavior, with characteristic times of 578 and 5670 s. The relative contributions of the two components were 57.3% and 42.7%, respectively. Comparing the amplitude of the short time constant component at 1.7 K with the signal at 4.2 K, both of which had similar growth times, indicates an enhancement of 3.78. Assuming a simple Boltzmann scaling of the electron spin polarization, lowering the temperature from 4.2 to 1.7 K should just change the polarization by a factor of 1.25.

There are at least two contributions to this additional enhancement. First, the efficiency of coupling the laser to the silicon crystal is improved at low temperature, as the liquid helium bath enters a superfluid phase below 2.17 K and consequently bubbles in the bath are eliminated. At 4.2 K, we in fact observe substantial bubbling of the liquid helium at the inner window of the Dewar. These bubbles reduce the effective coupling of the light onto the sample. In addition, the electron spin \( T_1 \) is longer at low temperature [7], and the interplay with the optically excited carriers could enhance the polarization [29,30].
natural abundance silicon (doping concentration of polarization (DNP) experiment on phosphorus donors in observed in a recent microwave-induced dynamic nuclear spins\[31\]. Alternatively, the hyperpolarization could be interaction, resulting in the hyperpolarization of the nuclear trapping process is most likely mediated by the hyperfine that when spin-orbit interactions are weak, as in silicon, this up by the optically excited conduction band electrons\[32,33\].

4.2 K (Fig. 2). A similar biexponential growth has been at 1.7 K was not measured beyond 2.5 h polarization time at high magnetic fields\[31\], and the electron pairs in these form the bound singlet. Sekiguchi it is necessary to flip either the donor or the free electron to spin polarization (of the donors and free electrons) is high, donor-bound excitons also form singlets. When the electron spin polarization (of the donors and free electrons) is high, it is necessary to flip either the donor or the free electron to form the bound singlet. Sekiguchi et al. have suggested that when spin-orbit interactions are weak, as in silicon, this trapping process is most likely mediated by the hyperfine interaction, resulting in the hyperpolarization of the nuclear spins\[31\]. Alternatively, the hyperpolarization could be produced by cross relaxation of the donors, as they are heated up by the optically excited conduction band electrons\[32,33\].

The detailed physics underlying the optical hyperpolarization process is not well understood. Honig and co-workers have previously shown that the negatively ionized donors produced by spin trapping of optically excited conduction band electrons form singlet states at high field\[29\]. Similarly, optical experiments have shown the creation of donor-bound excitons at both low\[14\] and high magnetic fields\[31\], and the electron pairs in these donor-bound excitons also form singlets. When the electron spin polarization (of the donors and free electrons) is high, it is necessary to flip either the donor or the free electron to form the bound singlet. Sekiguchi et al. have suggested that when spin-orbit interactions are weak, as in silicon, this trapping process is most likely mediated by the hyperfine interaction, resulting in the hyperpolarization of the nuclear spins\[31\]. Alternatively, the hyperpolarization could be produced by cross relaxation of the donors, as they are heated up by the optically excited conduction band electrons\[32,33\].

The long time component of the growth curve observed at 1.7 K was not measured beyond 2.5 h polarization time at 4.2 K (Fig. 2). A similar biexponential growth has been observed in a recent microwave-induced dynamic nuclear polarization (DNP) experiment on phosphorus donors in natural abundance silicon (doping concentration of 6.5 × 10^{16} \text{ cm}^{-3}) at 4.6 T and temperatures of 200 mK and 1 K\[34\]. They observed a short time scale of 15 s and a longer time scale of 1100 s in their experiment. Though they attribute the presence of the longer time scale to the presence of ^29\text{Si} spins around the phosphorus donors, this is unlikely to be the case here, as a similar biexponential behavior is observed in our isotopically enriched silicon-28 crystal.

We performed spin-echo experiments to measure the coherence time of the ^31\text{P} nuclear spins. Following 200 s of laser irradiation, a Hahn-echo sequence (\(\pi/2 - \tau - \pi - \tau - \text{acquire}\)) was used to measure the nuclear spin coherence time (Fig. 3). By recording the echo signal while varying the delay time (\(\tau\)), we measured the signal decay at both 4.2 and 1.7 K as shown in Fig. 3. We fit the data with a single exponential decay and measured nuclear spin \(T_2\) values of 56 and 421 ms at 4.2 and 1.7 K, respectively.

As the magnetic field is increased, it is observed that the electron spin \(T_1\) at low temperature and high field gets

FIG. 2 (color online). Buildup on the nuclear spin polarization by 1047 nm laser irradiation for up to ~10 h, at 1.7 and 4.2 K temperature, respectively. The red lines represent a biexponential fit with time constants, \(\tau_1 = 5670 \text{ s}\) and \(\tau_2 = 578 \text{ s}\) at 1.7 K, and an exponential fit with \(\tau = 577 \text{ s}\) at 4.2 K. The star represents a thermal polarization measurement (laser off) for ~10 h, at 1.7 K, where no polarization could be observed.

FIG. 3 (color online). Nuclear spin coherence time \(T_2\) measured with the Hahn echo at 4.2 K temperature (open squares); Hahn echo at 1.7 K (full circles); and CPMG pulse sequence at 1.7 K (open hexagons). All data were measured in 6.7 T field, with 200 s of optical polarization provided by a 1047 nm, 100 mW, above-gap laser.
significantly shorter, since $T_1 T_2^{-1} \propto B^4$ as the result of a direct single-phonon relaxation process [36–39]. The hyperfine interaction is field independent, so the main factor limiting the nuclear $T_2$ is the electron $T_1$ carrying the $^{31}\text{P}$ spin to the electron spin $|\uparrow,\downarrow\rangle$ manifold [40] (see Supplemental Material [20] for details). In the presence of light, the $T_1$ is further shortened by up to 2 orders of magnitude due to trapping and reemission, with $T_1$ on the order of 2 ms in the presence of light and almost 20 ms in the dark at 8.56 T [11,35].

Here the electron spin undergoing $T_1$ relaxation induces an effective $T_2$ process on the nuclear spin with time constant $T_2^{en}$ (see Supplemental Material [20]). If $AT_1^{\pi} \gg 1$, then

$$T_2^{en} = \frac{T_1^{\pi}}{p_\uparrow},$$

where $p_\uparrow$ is the probability for the electron to be in the excited state. The high temperature limit of this model has been applied to explain the nuclear $T_2$ [1]. If we assume that the experimentally observed nuclear $T_2(T)$ combines two independent effects $1/T_2(T) = 1/T_2' + p_\uparrow(T)/T_1(T)$, where $T_2'$ is temperature independent, then we obtain $1/T_2' \leq 1/T_1(1.7 \text{ K})$. This in turn puts an upper bound on the electron relaxation time $T_1(4.2 \text{ K}) < p_\uparrow(4.2 \text{ K})/(T_2(1.7 \text{ K})T_2(4.2 \text{ K})/(T_2(1.7 \text{ K}) - T_2(4.2 \text{ K})))$ or $T_1(4.2 \text{ K}) \leq 6.7 \text{ ms}$, where we have assumed that $p_\uparrow$ is given by the equilibrium thermal probability. This value is shorter than the $T_1^{\pi} = 20 \text{ ms}$ measured in the dark at 8.56 T [35].

In order to minimize the effect of environmental fluctuations, we applied a Carr-Purcell-Meiboom-Gill (CPMG) refocusing pulse sequence to extend the nuclear spin coherence time. In the CPMG sequence, the single $\pi$ pulse of the Hahn echo is substituted with a series of $\pi$ pulses that are $90^\circ$ out of phase with respect to each other, with a $\tau$ spacing of 2 ms. The resulting echo decay is presented in Fig. 3, with a single exponential fit to the data returning $T_2 = 1.2 \text{ s} \pm 0.1 \text{ s}$, a factor of almost 3 improvement in nuclear spin coherence time. This is similar to the value of 1.75 s measured previously by usingENDOR at 5.5 K [1].

This CPMG sequence will refocus interactions between the phosphorus nucleus and other spins (or fields) that are fluctuating on a time scale longer than a few hundred hertz. The sequence will thus refocus fluctuations due to distant donor electrons, silicon nuclei (the silicon-phosphorus nuclear dipolar coupling is very small and does not play an important role here [41]), and static field inhomogeneities. The phosphorus nuclear dipolar coupling is not refocused but is only about 1.5 MHz for our donor concentration, and the dominant contribution from the electron $T_1^{\pi}$ induced nuclear $T_2$ is also not refocused by the CPMG sequence.

Last, we confirmed the long $T_1$ relaxation times, at 4.2 and 1.7 K temperatures. Figure 4 shows $T_1$ data for two experiments, a 200 s laser polarization pulse, followed by in the first case a delay time $\tau$ and a $\pi/2$-readout pulse and in the second case $\pi-\tau-\pi/2$ pulse sequence. The only difference between the two runs is the initial nuclear state. If most of the population is localized in the $|\downarrow,\uparrow\rangle$ state, applying a $\pi$ pulse before the readout pulse will move it to the $|\downarrow,\downarrow\rangle$ state [Fig. 1(b)]. The $T_1$ relaxation should not depend on the initial state, which is confirmed in Fig. 4. In addition, we observe that the spin-lattice relaxation time not only increases at lower temperatures but also exceeds the measuring times of our setup; no visible decay was observed after waiting for delay time $\tau = 4.5 \text{ h}$ (Fig. 4).

In conclusion, the results presented here show the first single FID measurement of the local magnetic fields seen by $^{31}\text{P}$ nuclear spins in a dilute crystal of $^{28}\text{Si}$. The negative $^{31}\text{P}$ polarization is $>11\%$ at 4.2 K, and $>64\%$ at 1.7 K and 6.71 T. It was accomplished by directly illuminating the sample with an above-gap 1047 nm laser for over 5 h at 1.7 K and 2.7 h at 4.2 K. We were able to extend the $T_2$ relaxation time to 1.2 s at 1.7 K and confirm an extremely long $T_1$ of the $^{31}\text{P}$ nuclear spins at 1.7 K which could not be determined within the time scale of this experiment.

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The processes of extending the $^{31}$P $T_2$ by moving the polarized system to higher temperature where the electron becomes much less important to the defect yields an average nearest neighbor silicon hyperfine coupling of about 200 kHz, average nearest neighbor silicon nuclear dipolar coupling of about 100 Hz. We are in the processes of extending the $^{31}$P $T_2$ by moving the polarized system to higher temperature where the electron becomes much less important to the defect $T_2$. Given the isotopic enrichment of 99.9954% for the silicon-28, we assume that the residual 0.0046% is purely silicon-29 as the concentration of silicon-30 has been measured to be about 40 times lower than that of silicon-29 in the Avogadro samples. Assuming a uniform distribution of spins, this yields an average nearest neighbor silicon hyperfine coupling of about 200 kHz, average nearest neighbor silicon nuclear dipolar coupling of about 7 Hz, and average nearest neighbor silicon-phosphorus nuclear dipolar coupling of 100 Hz.

See Supplemental Material at for http://link.aps.org/supplemental/10.1103/PhysRevLett.113.267604, which includes Refs. [21–26], for theoretical description of the nuclear spin $T_2$ due to the electron spin undergoing $T_1$ relaxation model, the data on the nuclear $T_2$ relaxation with the laser on, and the technical description of the optical, NMR, and cw-ESR setup including a short sample description.