Dynamic nuclear polarization in intermediately-doped single crystal silicon

A. E. Dementyev

*Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, MA 02139

D. G. Cory

Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139 and Perimeter Institute for Theoretical Physics, Waterloo, ON N2L 2Y5, Canada

C. Ramanathan*

*Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139

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Abstract

We report the hyperpolarization of $^{29}\text{Si}$ in n-doped silicon crystals, with dopings concentrations in the range of $1-3 \times 10^{17}$ cm$^{-3}$. The sign of the enhancement and its frequency dependence suggest that the $^{29}\text{Si}$ spins are directly polarized by donor electrons via an Overhauser mechanism within exchange-coupled donor clusters. Nuclear polarization enhancement is observed within clusters where the exchange energy is comparable to the donor hyperfine interaction. However the donor nuclei do not appear to be directly involved in the hyperpolarization of the silicon spins. In a 2.35 T magnetic field at 1.1 K, we observed a DNP enhancement of $244 \pm 84$ resulting in a silicon polarization of $10.4 \pm 3.4 \%$ following two hours of microwave irradiation.

*Please address correspondence to: sekhar@mit.edu
I. INTRODUCTION

Silicon has a number of appealing properties for spin-based applications in the emerging fields of spintronics and quantum information processing. In particular spin-based qubits using phosphorus-doped silicon are a subject of extensive experimental effort. At low temperatures the electron spins in phosphorus-doped silicon have been shown to have very long coherence times. In natural silicon the coherence times are limited by the configurational broadening due to the $^{29}$Si nuclear spin environment [1, 2]. This broadening can be narrowed, in principle, either through isotopic purification or by polarizing the nuclear spins.

It is possible to enhance the nuclear spin polarization in silicon by polarization transfer from adjacent electron spins through microwave irradiation of the coupled electron-nuclear spin system. For $g$=2 electrons and $^{29}$Si nuclei the maximum enhancement achievable is 3350. There have been a number of experimental efforts to dynamically polarize the $^{29}$Si nuclear spins in silicon. To date microwave-induced DNP experiments have been performed either at high temperatures or low magnetic fields [3–7]. The highest silicon polarization obtained in this regime was 4.6 % using the integrated solid effect [5].

In single crystal silicon, microwave-induced dynamic nuclear polarization (DNP) is usually mediated by donor electrons (or holes), and the DNP mechanism thus depends on the doping concentration. At low doping concentrations and low temperatures the donor electrons are localized at the individual donor sites. These sites are sparsely distributed, and essentially isolated from each other. The sample is an insulator, and its ESR spectrum shows well resolved hyperfine splittings [8]. The DNP is driven by the solid effect [9], which relies on the admixing of the nuclear spin eigenstates due to anisotropic hyperfine interactions. However at the low temperatures required to obtain large electron spin polarizations the electron spin $T_1$ in silicon becomes extremely long and very little enhancement is obtained. Hayashi et al. have tried to improve DNP efficiency in this regime using optically excited carriers to shorten the electron spin $T_1$, with some success [7].

At high doping concentrations, the ESR spectrum collapses to a single exchange-narrowed line before the system undergoes a metal-insulator transition [8]. (The critical concentrations for phosphorus- and antimony-doped silicon are in the region of $3 - 4 \times 10^{18}$ cm$^{-3}$ [10].) The DNP in this case is mediated by the Overhauser effect, where the fluctuating hyperfine interaction leads to electron-nuclear cross-relaxation processes [11]. In this case the electron
spin $T_1$ is so short that it is very difficult to saturate the ESR transitions and achieve large DNP enhancements [3].

Intermediate between these two regimes, the properties of the system change dramatically as a function of the doping concentration. At liquid helium temperatures the electron spin $T_1$ in phosphorus doped silicon changes by 8 orders of magnitude as the doping concentration is varied from $5 \times 10^{16}$ cm$^{-3}$ to $6 \times 10^{17}$ cm$^{-3}$ [12]. Thus by changing the donor concentration it may be possible to tailor the $T_1$ of the sample so that appreciable DNP can be achieved without excessive amounts of microwave power. We report here on the hyperpolarization of $^{29}$Si in both phosphorus- and antimony-doped silicon wafers, where the doping concentration is in this intermediate regime.

Dynamic polarization of silicon nuclei has also been demonstrated in amorphous silicon [13], and in silicon microparticles [14]. The electron spins responsible for the DNP in these experiments are the dangling bonds at the silicon surface. The DNP mechanism is thermal mixing between the electron dipolar system and the nuclear Zeeman system. The coherence times of the electron spins in these systems are however typically significantly shorter than in low-defect single crystal systems.

II. RESULTS AND DISCUSSION

Figure 1 shows the result of a DNP experiment using an antimony-doped sample. The enhanced polarization is opposite to the thermal equilibrium polarization. The experiments were performed at 2.35 T at a temperature of 1.4 K. The thermal electron spin polarization is 81 % while the thermal $^{29}$Si polarization is 0.034 %. The observed enhancement of 20 corresponds to a silicon polarization of 0.68 %. We used a 100 mW Gunn diode source (Millitech) tuned to 66 GHz, coupled to a standard microwave gain horn to drive the electron spin transitions [15]. The experimental scheme is shown in the inset of the figure. The CW microwaves are always on. We apply a saturation train of $\pi/2$ pulses to initially destroy the nuclear spin polarization. Following a variable delay during which the nuclear spin signal grows due to DNP, the polarization is monitored by a single nutation pulse (denoted by $\alpha$).

Figure 2 shows the build up of the silicon polarization under different conditions. Note that a 90 deg pulse is used to monitor the thermal silicon polarization, while a 5 deg pulse is used to monitor the silicon polarization after DNP, which scales the signal by a factor
FIG. 1: DNP enhancement of 20 obtained following microwave irradiation of an antimony-doped silicon wafer \((2.5 \times 10^{17} \text{ cm}^{-3})\) at 1.4 K. Note that the hyperpolarized signal is opposite to the thermally polarized signal. The inset shows the basic DNP experiment. (color online)

of 11.5. The original enhancement of 20 is increased by approximately a factor of 2 when we use a 1 W microwave source instead of the 100 mW source. This demonstrates that we were unable to saturate the ESR transitions effectively with the lower powered source. The \(^{29}\text{Si}\) signal is still increasing after 2 hours of microwave irradiation. However the hold time of our cryostat reduced from 4 hours to about 2 hours with the increased microwave power and lower temperature. Clearly an increased microwave irradiation time would allow us to achieve even higher nuclear spin polarizations. The figure also shows that reducing the temperature of the system from 1.4 K to 1.1 K further increases the polarization as expected.

We replaced the microwave horn with a tuned cylindrical TE\(_{011}\) cavity to increase the strength of the applied microwave magnetic field. The RF coil was located just below the cavity, and the sample was physically moved from the cavity to the coil following microwave irradiation. Since the \(T_1\) of the silicon nuclei is on the order of hours, there is little loss of polarization during this process. At a temperature of 1.1 K we obtained a DNP enhancement
FIG. 2: Build-up of $^{29}$Si polarization in antimony-doped silicon ($2.5 \times 10^{17}$ cm$^{-3}$). The enhancement obtained with the 100 mW source is clearly power-limited. With the 1W microwave source the hold time of the cryostat shortened from 4 hours to 2 hours. A 5 deg pulse was used to monitor the polarization in the DNP experiments while a 90 deg pulse was used in the thermal equilibrium situation (color online).

of $244 \pm 81$ in phosphorus-doped silicon ($N_d \approx 2 \times 10^{17}$ cm$^{-3}$), shown in Figure 3 which corresponds to a silicon nuclear spin polarization of $10.4 \pm 3.4 \%$, the highest value reported to date. The thermal electron spin polarization is $90 \%$ under these conditions. We were unable to measure a thermal silicon signal from the 2.8 mg piece of silicon wafer that was used for the DNP. A second 2.1 mg piece of wafer was added to the sample, and the thermal signal shown in Figure 3 was recorded after 8 averages. The ratio of the measured signal intensities is $17.4 \pm 5.8$. The low signal to noise ratio in this thermal signal is responsible for the relatively large uncertainty in the enhancement factor and the final silicon polarization.

In order to probe the DNP mechanism, we recorded ESR spectra from the samples and monitored the DNP signal as a function of the microwave irradiation frequency. The changes in the ESR lineshape of doped silicon samples as a function of the doping concentration have been studied extensively [8]. Figure 4 shows the results of low temperature ($3.4$ K) X-band
FIG. 3: DNP of P-doped silicon ($N_D = 3 \times 10^{17}$ cm$^{-3}$) at 1.1 K. The sample is placed in a tuned TE$_{011}$ cylindrical resonator during the microwave irradiation, and then physically moved approximately 1 inch to the center of the RF coil where the polarization is measured. The DNP signal (1 average) was recorded from a 2.8 mg piece of silicon wafer. The thermal signal (8 averages) was recorded from a sample that also contained an additional 2.1 mg wafer fragment (total weight 4.9 mg). The ratio of the measured signal intensities is $17.4 \pm 5.8$, indicating a DNP enhancement of $244 \pm 81$ (color online).

ESR experiments on two of the samples studied. Given the random distribution of donors, the sample contains isolated donors as well as clusters of different sizes with an almost continuous distribution of exchange interaction strengths. The measured ESR signal is an incoherent sum of these different contributions [12]. The spectra in Figure 4 show several characteristic features of this sum. While the signal from the phosphorus-doped sample was obtained under rapid-passage conditions, the signal from the antimony-doped sample did not satisfy the rapid passage conditions, resulting in some lineshape distortions.

Phosphorus-31 is 100 % abundant and is a spin-1/2 nucleus with a donor hyperfine interaction of 117.5 MHz in silicon. The two isotopes of antimony, $^{121}$Sb and $^{123}$Sb are 57.4 % and 42.6 % abundant, have nuclear spin 5/2 and 7/2 and hyperfine interaction strengths of
FIG. 4: ESR spectra of phosphorus and antimony-doped silicon crystals obtained at X-band at a temperature of 3.4 K. The signal from the phosphorus-doped sample was obtained under rapid-passage conditions. The spectrum shows the two hyperfine resolved lines, the broad center line, and additional peaks that arise from donor clusters. The signal from the antimony-doped sample did not quite satisfy the rapid passage conditions, resulting in some lineshape distortions. The antimony doped sample shows the presence of 14 hyperfine resolved lines as well as the broad center line. We did not resolve the cluster peaks in this sample. (color online)

186.8 MHz and 101.5 MHz respectively [8]. As a result the spectra from the isolated donors show 2 resolved hyperfine peaks for phosphorus and 14 for antimony. In the phosphorus-doped sample, the small additional peaks in the spectra arise from exchange coupled clusters in which the exchange energy is much stronger than the donor hyperfine interaction [16]. If there are N strongly coupled donors the hyperfine interaction in the symmetric manifold of the donors is given by

$$\mathcal{H}_{hf}^S = \frac{A}{N} S_z \left( I_1^z + I_2^z + \ldots + I_N^z \right)$$

(1)

where $A$ is the hyperfine interaction of a single donor. For a cluster containing N strongly coupled phosphorus donors (spin 1/2), there are N+1 resolved ESR transitions. If the nuclear spins are unpolarized, the line intensities should follow a binomial distribution. For
strongly-coupled antimony clusters the spectra are much more complex given the presence of two isotopes with spin 5/2 and 7/2. These give rise to multinomial distributions. For example, for a pair of spin-5/2 $^{121}$Sb, we expect 21 lines, which would follow a triangular distribution for unpolarized nuclei. We did not resolve these peaks in the antimony-doped sample. Finally both spectra show the presence of a broad background signal spanning the width of the resolved hyperfine interactions. This background arises from exchange coupled clusters of two or more donors, where the exchange coupling is comparable to the donor hyperfine interaction [17–19]. The width of the background is about 60 G for the phosphorus-doped sample and about 350 G for the antimony doped sample, corresponding to 150 MHz and 875 MHz respectively for $g \approx 2$. The hyperfine coupling to the $^{29}$Si nuclei is not resolved and contributes an inhomogeneous linewidth of about 2.5 G to the spectra [8].

Figure 5 shows the DNP signal (amplitude normalized) as a function of the microwave irradiation frequency. The data were acquired with the 100 mW Gunn diode source. DNP enhancement is observed over a frequency range of about 200 MHz for the phosphorus-doped
silicon and about 1 GHz for the antimony-doped silicon, which is similar to the widths of the broad center lines in the ESR spectra in Figure 4. The figures do not show any features at the frequencies of the resolved hyperfine interactions for either sample. This suggests that the observed DNP is dominated by microwave irradiation of exchange-coupled clusters of donors, where the strength of the exchange coupling is comparable to the donor hyperfine coupling.

The sign of the enhancement does not change as we vary the microwave frequency, suggesting that an Overhauser mechanism is responsible for the enhancement. The maximum Overhauser enhancement is given by $-\gamma_e/\gamma_n$. Since both the electron and the silicon nucleus have negative gyromagnetic ratios, while the phosphorus and antimony nuclei have positive gyromagnetic ratios, the negative sign of the enhancement indicates a direct Overhauser enhancement of the silicon nuclei in both the phosphorus- and antimony-doped samples. Overhauser DNP has previously been observed in some charcoals in the presence of strong electron exchange interactions, where the ESR spectrum collapses to a single exchange-narrowed line [20].

The physics underlying the DNP process is the same for both phosphorus and antimony doped samples. Both are shallow donors and the electron Bohr radius ($\sim 2$ nm) is expected to be very similar. Thus, the strength of the exchange interaction depends on the spatial distribution of donors, which in turn depends on the donor concentration. The donor hyperfine interaction and the exchange energy of the cluster are important in determining the frequencies of the allowed ESR transitions, which is where the difference between the phosphorus and antimony samples is manifest.

III. MODEL SYSTEM

Here we want to describe a simple model to explain the Overhauser enhancement of the silicon nuclei in an exchange-coupled donor cluster (Figure 6). The goal of the model is to explain the initial growth and the frequency dependence of the DNP signal. For simplicity we consider a cluster of phosphorus donors, since the nuclear spins have $I = 1/2$. The simplest model required would seem to be a 5 spin model — containing two $^{31}$P donor nuclei, two electrons and a single $^{29}$Si nucleus that is located within the Bohr radius of one of the electrons. Since the Bohr radius of the electron in P-doped silicon is almost 2 nm, there are
FIG. 6: Schematic illustration of a two-donor cluster, showing the overlap of the electron orbitals with a number of $^{29}$Si nuclei (color online).

about 1700 silicon nuclei within this region. For natural abundance silicon this corresponds to about 80–100 $^{29}$Si nuclei in hyperfine contact with the electron. We additionally assume that both the donor and the $^{29}$Si hyperfine interaction can be approximated by an isotropic Fermi-Segre contact interaction. The Hamiltonian of the 5 spin system is

$$
\mathcal{H} = -\omega_e (S_z^1 + S_z^2) + J S_z^1 \cdot S_z^2 + D (2S_z^1 S_z^2 - S_x^1 S_x^2 - S_y^1 S_y^2) + \\
A_D (S_z^1 I_z^{D1} + S_z^2 I_z^{D2}) + \omega_D (I_z^{D1} + I_z^{D2}) + A S_z I_z - \omega_n I_z
$$

(2)

where $\omega_e$ is the electron Larmor frequency, $S^1$ and $S^2$ are the two electron spins, $I^{D1}$ and $I^{D2}$ are the donor nuclear spins, $I$ is the $^{29}$Si spins, $J$ is the exchange coupling strength, $D$ is the dipolar coupling between the electron spins, $A_D$ is the donor hyperfine coupling, $\omega_D$ is the Larmor frequency of the donor nuclei, $A$ is the hyperfine interaction with the $^{29}$Si nucleus and $\omega_n$ is the Larmor frequency of the silicon nucleus. Note that $\omega_e$, $\omega_D$ and $\omega_n$ are all positive. The exchange coupling is known to be antiferromagnetic in silicon ($J > 0$) [19]. Here we have neglected the nuclear dipolar coupling as it is much weaker than any of the other interactions in the system. It can be seen that the donor nuclei shift the energy levels, but always remain separable from the electrons. If the donor nuclei are unpolarized, we have a distribution over the corresponding electron spin energies. This distribution narrows as the donor nuclei become polarized. The $^{29}$Si spin also remains separable from
FIG. 7: Eigenstates of the 3-spin Hamiltonian shown in Equation 4, where $\alpha = \cos \frac{\theta}{2}$, $\beta = \sin \frac{\theta}{2}$, $\gamma = \cos \frac{\phi}{2}$, $\delta = \sin \frac{\phi}{2}$, $\tan \phi = \frac{-J_+}{2D+A/2}$, and $\tan \theta = \frac{-J_+}{2D-A/2}$. The dashed black lines show the allowed ESR transitions that are not excited by the applied microwaves. The solid blue lines show the allowed ESR transitions that are resonant with the applied microwave irradiation. The dotted red line indicates the hyperfine mediated cross-relaxation path leading to DNP. The energy levels shown in dark green correspond to the symmetric manifold while the levels shown in light green correspond to the asymmetric manifold. We have labeled the states such that $S_z |0\rangle = -\frac{1}{2} |0\rangle$, and $S_z |1\rangle = \frac{1}{2} |0\rangle$. The figures also shows the offset ESR frequencies $\omega - \omega_e$ as a function of the exchange coupling for the lower electron spin manifolds for $\delta = 0$ and 60 MHz. For $\delta = -60$ MHz the curves are almost identical to those for $\delta = +60$ MHz. We used $A = 4$ MHz, $D = 0$ MHz, and $\omega_n = 20$ MHz. (color online).
the electronic spin states under this Hamiltonian. We can reduce the dimensionality of the problem while capturing the essential physics if we replace the above Hamiltonian by a 3 spin Hamiltonian where the two electrons spins may be inequivalent (depending on the state of the associated $^{31}$P nuclear spin).

$$H = (-\omega_e - \delta) S_x^1 + (-\omega_e + \delta) S_x^2 + J \hat{S}_1^z \cdot \hat{S}_2^z + D (2S_x^1 S_x^2 - S_y^1 S_y^2 - S_z^1 S_z^2) + A S_z^1 I_z - \omega_n I_z$$ (3)

which can in turn be re-written as

$$H = -\omega_e \left(S_x^1 + S_x^2\right) - \delta \left(S_z^1 - S_z^2\right) + J || S_z^1 S_z^2 +$$

$$J \bot \left(S_x^1 S_x^2 + S_y^1 S_y^2\right) + \frac{A}{2} \left(S_z^1 + S_z^2\right) I_z +$$

$$\frac{A}{2} \left(S_z^1 - S_z^2\right) I_z - \omega_n I_z$$ (4)

where $J || = J + 2D$ and $J \bot = J - D$. Either the first or the second term is always zero, depending on the symmetry of the electron spin states. In the symmetric manifold $S_z^1 = S_z^2 = \pm 1/2$ and $S_z^1 - S_z^2 = 0$, while in the antisymmetric manifold $S_z^1 = -S_z^2 = \pm 1/2$, and $S_z^1 + S_z^2 = 0$. There are 4 levels in the symmetric manifold, two corresponding to $S_z^1 + S_z^2 = 1$ and two corresponding to $S_z^1 + S_z^2 = -1$.

The antisymmetric (or central) manifold has $S_z^1 + S_z^2 = 0$. The structure of this manifold depends on the relative magnitudes of $A$, $\delta$ and $J \bot$. The eigenstates are shown in Figure 7. The corresponding eigenenergies are

$$E_1 = \omega_e + \frac{\omega_n}{2} + \frac{A}{4} + \frac{J ||}{4}$$ (5)

$$E_2 = \omega_e - \frac{\omega_n}{2} - \frac{A}{4} + \frac{J ||}{4}$$ (6)

$$E_3 = \frac{\omega_n}{2} + \frac{\omega^+_e + \omega^-_e}{2} - \frac{J ||}{4}$$ (7)

$$E_4 = -\frac{\omega_n}{2} + \frac{\omega^+_e - \omega^-_e}{2} - \frac{J ||}{4}$$ (8)

$$E_5 = \frac{\omega_n}{2} - \frac{\omega^+_e + \omega^-_e}{2} - \frac{J ||}{4}$$ (9)

$$E_6 = -\frac{\omega_n}{2} - \frac{\omega^+_e - \omega^-_e}{2} - \frac{J ||}{4}$$ (10)

$$E_7 = -\omega_e + \frac{\omega_n}{2} - \frac{A}{4} + \frac{J ||}{4}$$ (11)

$$E_8 = -\omega_e - \frac{\omega_n}{2} + \frac{A}{4} + \frac{J ||}{4}$$ (12)

where $\omega^+_e + \omega^-_e = \sqrt{(2\delta - \frac{A}{2})^2 + J \bot^2}$ and $\omega^+_e - \omega^-_e = \sqrt{(2\delta + \frac{A}{2})^2 + J \bot^2}$. 
In our system $A \leq 4$ MHz is the hyperfine coupling to the silicon nuclear spin. The exchange coupling in different clusters range continuously from near zero to $J \approx 100$ GHz [18], and depending on the state of the phosphorus donor nuclei, $\delta$ takes on the value of -60 MHz ($\downarrow\downarrow$), 0 MHz ($\downarrow\uparrow$ or $\uparrow\downarrow$) or 60 MHz ($\uparrow\uparrow$) which is half the hyperfine coupling to the phosphorus nuclei. The electron Zeeman frequency is 66 GHz. In the limit that $J_{\perp} \gg A, \delta$, the two exchange coupled electrons form singlet (levels 5 and 6) and triplet (levels 1, 2, 3, 4, 7 and 8) states as $\theta, \phi \rightarrow -\pi/2$. This is why the width of the broad ESR line scales with the hyperfine coupling strength. For intermediate values of the exchange coupling $J_{\perp} \gg A$, $J_{\perp} \sim \delta$ microwave irradiation of the electron spins can induce the transitions $1 \leftrightarrow 3$, $1 \leftrightarrow 5$, $2 \leftrightarrow 4$, $2 \leftrightarrow 6$, $3 \leftrightarrow 7$, $5 \leftrightarrow 7$, $4 \leftrightarrow 8$ and $6 \leftrightarrow 8$ shown in Figure 7. The deviation of the ESR frequencies from the bare electron Larmor frequency $\omega - \omega_e$ are shown in the figure for the lower electron spin manifolds as a function of the strength of the exchange coupling.

The transition efficiency depends both on the applied microwave power and how well the microwaves are tuned to the particular transition. Since there is a random, quasi-continuous distribution of exchange coupling strengths in the sample, microwave irradiation at any frequency within the broad center line will be on-resonance for one of the transitions of an exchange-coupled pair. For that pair, the microwaves will also be nearly on-resonance for a second transition as well (for example 4 $\leftrightarrow$ 8 and 3 $\leftrightarrow$ 7). Since the strength of the applied $B_1$ field is on the order of about 10 MHz at most (1 W microwave power, low Q cavity), the other allowed transitions which are several tens of MHz off resonance are excited much less efficiently. In our experiments at 1.1 K and 2.35 T, only levels 7 and 8 are populated in thermal equilibrium, with almost equal populations, and the microwaves drives Rabi oscillations between the respective pairs of levels. Essentially we are then dealing with just a simple 4 level system similar to that used in standard textbook descriptions of the Overhauser effect in liquids [21].

We can consider these 4 levels (3,4,7 and 8 for example) represent a coupled spin-1/2 electron-nuclear system. The Hamiltonian of the system under microwave irradiation is given by

$$\mathcal{H} = \tilde{\omega}_e S_z + \tilde{\omega}_n I_z + \tilde{A} I_z S_z + 2\omega_1 \cos \omega t S_x$$

(13)
where
\[
\tilde{\omega}_e = \omega_e + \frac{\omega_e^+ - J_\parallel}{2},
\tag{14}
\]
\[
\tilde{\omega}_n = \omega_n + \frac{1}{2}\left(\omega_e^- - \frac{A}{2}\right),
\tag{15}
\]
\[
\tilde{A} = \omega_e^- + \frac{A}{2}.
\tag{16}
\]

If the microwaves are applied on-resonance \(\omega = \tilde{\omega}_e\), the electron spins are driven into saturation as \(\omega^2 T_1 T_2 > 1\). The degree of electron spin saturation is given by the saturation factor
\[
s = \frac{S_0 - \langle S_z \rangle}{S_0}.
\tag{17}
\]
The electron spin \(T_1\)'s of both the resolved hyperfine lines as well as the broad center line have been measured at X-band to be about 100 \(\mu s\) at 1.1 K for P-doped Si with \(N_D = 3 \times 10^{17}\) cm\(^{-3}\). The electron \(T_1\) is concentration dependent in these samples. It is the onset of exchange-mediated effects that is responsible for the dramatic change in \(T_1\) with doping concentration in the intermediate doping regime. Isolated donors relax via spin diffusion to fast relaxing centers in the lattice, while exchange coupled pairs and clusters of spins relax to the lattice via the exchange reservoir \cite{22}.

As the microwaves saturate the electron spin populations, the contact hyperfine interaction couples the relaxation dynamics of the two spin systems, and alters the populations of the nuclear spin. The dynamics of the nuclear spin polarization are given by \cite{21}
\[
\frac{d\langle I_z \rangle}{dt} = -\frac{1}{T} \left\{ \langle I_z \rangle - I_0 \left(1 - s \frac{\gamma_e}{\gamma_n}\right) \right\},
\tag{18}
\]
where \(I_0\) is the thermal equilibrium nuclear spin polarization, and we have used the fact that \(I = S = 1/2\) and that the thermal electron spin polarization \(S_0 = (\gamma_e/\gamma_n)I_0\). The time constant \(T\) is given by \cite{21}
\[
\frac{1}{T} = \frac{A^2}{2} \frac{\tau_2}{1 + (\omega_e - \omega_n)^2 \tau_2^2} \approx \frac{A^2}{2\omega_e^2 \tau_2},
\tag{19}
\]
where \(A\) is the hyperfine coupling strength and \(\tau_2\) is the correlation time of the transverse components of the electron spin. We have assumed here that there are no other sources of nuclear spin relaxation in these samples.

Table I shows the parameters obtained from fitting the data for antimony-doped silicon in Figure 2 to Equation 18, as well as the calculated saturation factor \(s\) and the correlation
### TABLE I: Parameters obtained by fitting the data in Figure 2 to Equation 18, using $A = 1$ MHz.

The amplitude of the DNP data was multiplied by 11.5 to account for the smaller flip angle pulsed used.

| temp | T  | $I_0(1 - s\gamma_e/\gamma_n)$ | s | $\tau_2 = A^2T/2\omega_e^2$ | $f_1 = \omega_1/2\pi$ | microwave source |
|------|----|-------------------------------|---|-----------------------------|------------------------|-----------------|
| 1.4 K | 10839 s | 1.08 x 10^5 | 0 | 32 ns | 0 | none |
| 1.4 K | 7593 s | -1.78 x 10^6 | 0.005 | 22 ns | 2.2 MHz | 100 mW Gunn |
| 1.4 K | 3400 s | -2.79 x 10^6 | 0.008 | 10 ns | 10 MHz | 1 W Impatt |
| 1.1 K | 3807 s | -3.53 x 10^6 | 0.008 | 11 ns | 10 MHz | 1 W Impatt |

The correlation time $\tau_2$ assuming $A \approx 1$ MHz. In the absence of microwave irradiation $\tau_2^0 \approx 32ns$. This corresponds to a 5 MHz exchange interaction between clusters, which is the dominant source of these fluctuations, in good agreement with the ESR and DNP experiments. Feher observed that the four most strongly-coupled silicon sites have hyperfine interactions ranging from 1–3 MHz for antimony-doped silicon, though the variation is not monotonic with distance in the immediate vicinity of the donor [8]. At greater distances the interaction approximately falls off as $\exp(-r/r_0)$ where $r_0 \approx 2$ nm is the Bohr radius of the donor electron. A hyperfine coupling of 1 MHz indicates that the nuclear spins are a polarized within one Bohr radius of the donor. If the nuclear spins were polarized at a greater distance from the donor, the hyperfine interaction would be weaker, and the correlation time $\tau_2$ would be correspondingly shorter. This would require a much stronger exchange interaction to explain the observed DNP dynamics. The correlation time is seen to get shorter as the microwaves power is increased, as the microwaves modulate the electron spins. In Table I we estimate the strength of the applied microwave field assuming

$$\frac{1}{\tau_2} = \frac{1}{\tau_2^0} + \omega_1.$$  \hspace{1cm} (20)

The saturation factors are quite low in these experiments. The use of the cavity in the experiments shown in Figure 3 is responsible for the significant increase in the saturation factor and the observed DNP enhancement.

Assuming a uniform distribution of donors, the average distance between donors is on the order of 15 nm for a donor concentration of $3 \times 10^{17}$ cm$^{-3}$. Given an electron Bohr radius of 2 nm, we see that a majority of the nuclei are not in hyperfine contact with a donor, and spin diffusion is essential to polarizing these nuclei [23]. The spin diffusion coefficient of natural
abundance silicon is about $1 \times 10^{-14}$ cm$^2$/s or 1 nm$^2$/s [7]. Thus the time take to transport the polarization the distance of 5–6 nm, required to polarize all the nuclear spin, is on the order of a few tens of seconds and is not the dominant timescale in these experiments.

In summary, we have achieved high $^{29}$Si polarization in both phosphorus- and antimony-doped single crystal silicon. The $^{29}$Si spins are directly polarized by donor electrons via an Overhauser mechanism within exchange-coupled donor clusters. The physics underlying the DNP process is the same for both donors. Our results indicate that the key to achieving higher polarization in these samples is to improve the efficiency with which we saturate the electron spin polarization, as we did when using a resonant cavity for the microwaves.

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