Optical and dynamic nuclear polarization of $^{29}$Si nuclei via photoexcited triplet states of oxygen-vacancy complexes in isotopically controlled silicon


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Optical and dynamic nuclear polarization of $^{29}$Si nuclei under saturation of the electron paramagnetic resonance (EPR) transitions of the photoexcited spin $S=1$ states (Si-SL1 centers) of the oxygen−vacancy complexes (A-centers) have been investigated using silicon single crystals with various $^{29}$Si nuclear abundances. The optical nuclear polarization alone led to the $^{29}$Si nuclear polarization enhancement by a factor of $\sim 500$ in the magnetic fields below 50 mT, and such enhancement was found to decrease significantly in the stronger fields up to 300 mT. On the other hand, saturation of the EPR lines of Si-SL1 centers having the electron spin polarization of 70−80% was transferred successfully to surrounding $^{29}$Si nuclear spins to achieve the overall $^{29}$Si nuclear spin polarization of $\sim 6.4\%$, and a method to increase up to 13−15% is proposed. The optimum condition to achieve such a high degree of nuclear polarization was found by systematic investigations of the dynamic nuclear polarization mechanisms.

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I. INTRODUCTION

Highly developed silicon technology, especially the fabrication of isotopically controlled bulk and layered silicon single crystals, is expected to open the next stage for silicon-based quantum information processing devices. Many of these applications employ electron and/or nuclear spins as qubits and require high spin polarization, i.e., initialization, at the start of quantum information processing and long coherence times for successful completion of the quantum algorithms. While the isotopic purification of host silicon matrix to eliminate background $^{29}$Si stable isotopes of nuclear spin $I = 1/2$ is proven essential for achieving the large polarization and long coherence times of electron and nuclear spins in silicon, there are schemes that take advantage of $^{29}$Si nuclear spins as qubits and thanks especially to the recent experimental demonstration of coherent quantum information transfer into and out of $^{29}$Si nuclear spins in silicon, exploration of physics leading to the high $^{29}$Si nuclear spin polarization becomes important to reach at least 5% for implementation of the efficient algorithmic cooling protocol.

The first, forced polarization of $^{29}$Si nuclei was demonstrated by Abragam et al. by microwave irradiation of a phosphorus-doped silicon single crystal. Here, they achieved the polarization of 0.048%, which corresponded to the enhancement by a factor of 30 with respect to its thermal equilibrium value. An optical nuclear polarization (ONP) approach started by Lampel in 1968 reached 0.03% in 1982 and 0.25% in 2005. Electron paramagnetic resonance- (EPR-) induced dynamic nuclear polarization (DNP) with lightly phosphorus-doped ($\sim 10^{15}$ cm$^{-3}$) silicon achieved $^{29}$Si polarization of 1.45%, and this was limited by the long relaxation time of electrons bound to phosphorus donors ($\sim 3 \times 10^3$ s at 1.2 K). In similar DNP studies using lithium-doped silicon, the $^{29}$Si polarization was limited to 0.72% due to the inhomogeneous broadening of EPR absorptions of electrons bound to isolated lithium and lithium-forming complexes with oxygen. DNP of $^{29}$Si with silicon microparticles has reached 2%, and heavily doped ($\sim 10^{17}$ cm$^{-3}$) phosphorus silicon bulk single crystals has achieved an impressive 10.4%. While the physics leading to very high $^{29}$Si polarization in microparticles and in heavily doped silicon is very interesting, employment of lightly doped silicon single crystals are preferred strongly for quantum information processing in order to retain the coherence time as long as possible. The present work shows a systematic investigation of dynamic $^{29}$Si nuclear polarization using electron spins bound to photolithography vapor-deposition (O-V) spin-triplet (SL1) centers leading to the maximum $^{29}$Si nuclear polarization of $\sim 6.4\%$. The concentration of SL1 is low, of the order of $10^{15}$ cm$^{-3}$, and they exist only during the optical irradiation for initialization. As soon as the illumination is terminated, they decay to spin-singlet centers and do not act as sources of decoherence of surrounding spins.

Early experimental and theoretical investigations of DNP in solids have shown that the maximum DNP degrees that can be achieved by the Overhauser effect and solid effect is equal to the equilibrium electron Boltzmann polarization of paramagnetic spin $S = 1/2$ centers. The maximal DNP enhancement $E$, the ratio of DNP degree $P_N$ to the equilibrium Boltzmann nuclear polarization $P_{NO}$, is given by $E_{\text{max}} = P_N / P_{NO} = P_{NO} / P_{NO} = \gamma_e / \gamma_N = 3310$ for silicon, where $\gamma_e = 28$ MHz/mT and $\gamma_N = 8.46$ kHz/mT are the electron and $^{29}$Si nuclear gyromagnetic ratios, respectively.

To achieve the highest $P_N$, the DNP experiments should be performed at low temperatures and at high magnetic fields. However, as mentioned above, the DNP experiments performed with phosphorus-doped silicon have shown that the efficiency of DNP process is limited by the long electron
spin-lattice relaxation time of paramagnetic phosphorus donors at low temperatures. The DNP enhancement at low temperatures was demonstrated by saturating the Zeeman-split electron spin levels of phosphorus donors at the magnetic field \( B = 320 \text{ mT} \), \( T = 12 \text{ K} \), but \( E \) was much smaller at lower \( T \) due to the long electron relaxation time and at higher \( T \) due to ionization of the phosphorus donors.

The idea to use the triplet centers for nuclear polarization has been suggested and realized in the experiments on ONP of protons in molecular crystals without applying the resonance microwave field. Later, experiments on DNP using the EPR saturation of the photoexcited triplet centers in molecular crystals were performed and a new method of proton DNP using electron spin-locked effect was suggested.

The photoexcited triplet (spin \( S = 1 \)) centers in silicon, such as photoexcited neutral O-V complexes (Si-SL1), Al-V complexes, Sn-V complexes, P-V complexes, carbon-related centers, and divacancies, show advantages for DNP over the traditional spin \( S = 1/2 \) paramagnetic centers. Such centers are characterized by nonequilibrium populations of magnetic sublevels with different electron spin projections \( m_S = \pm 1, 0, \) and \( -1 \), resulting from the spin-selective transitions from one of the three triplet levels to the spin-singlet ground state.

### II. Experimental

The experiments were performed with \( n \)- and \( p \)-type Czochralski-grown silicon crystals containing 0.59, 4.7, and 99.2\% of \( ^{29}\text{Si} \) isotope. Si samples doped with phosphorus \( (N(P) \approx 10^{15} \text{ cm}^{-3}) \) and containing 0.59 and 99.2\% of the \( ^{29}\text{Si} \) isotopes were irradiated at room temperature by \( \gamma \)-rays from the \( ^{60}\text{Co} \) source with the dose of \( 8 \times 10^{15} \text{ \gamma/cm}^2 \). In addition, two samples of \( n \)-Si (\( N(P) \approx 5 \times 10^{16} \text{ cm}^{-3} \)) and high-resistance \((\approx 1000 \Omega \text{ cm})\) \( p \)-type Si with the natural (4.7%) abundance of the \( ^{29}\text{Si} \) isotopes were irradiated by 1-MeV electrons with the dose of \( 10^{18} \text{ e/cm}^2 \) at room temperature.

A JEOL JES-RE3X X-band EPR spectrometer was used for detection of the EPR signals and for DNP of \( ^{29}\text{Si} \) nuclei through the saturation of EPR transitions at different values of magnetic field \( B_{sat} \). The experiments were performed at the temperatures between 3.8 and 100 K using an Oxford Instruments (ESR900) helium gas flow cryostat. To create the excited spin \( S = 1 \) states of \( A \)-centers, samples placed in a cylindrical TE011 mode cavity were illuminated with a \( \lambda = 1047\text{-nm} \) line from a 2W Nd:YLF laser or by white light from a 100-W halogen lamp.

DNP was induced by saturation of a particular EPR transition using the same EPR spectrometer with a maximum microwave power of 200 mW at a fixed microwave frequency of 9.05 GHz. The magnetic field modulation amplitude \( B_{mod} \), from \( 10^-2 \) to \( 1 \) mT, and microwave power were optimized for each investigated sample. The time of EPR saturation \( t \) varied from 10 min to 3 h.

After the EPR saturation, the sample was transferred from the EPR spectrometer to a CMX300 CP/MAS nuclear magnetic resonance (NMR) spectrometer. The transfer time was typically 2 min. The long \( ^{29}\text{Si} \) nuclear spin-lattice relaxation time \( T_{1N} > 1 \) h for all samples at room temperature allowed to separate the EPR saturation and NMR measurements in time and space without the loss of signal intensity. To prevent fast nuclear relaxation and loss of nuclear polarization in the Earth's magnetic field, the samples were transferred to the NMR spectrometer using a small permanent magnet.

The \( ^{29}\text{Si} \) NMR signal was detected at room temperature using Fourier-transformed free-induction decay after a \( \pi/2 \) pulse with a magnetic field of 7 T, corresponding to the \( ^{29}\text{Si} \) NMR frequency of 60 MHz. The pulse length and the acquisition delay time after the \( \pi/2 \) pulse were 9 \( \mu\text{s} \) and 35 \( \mu\text{s} \), respectively. The nuclear polarization degree and enhancement \( E \) were determined by comparing the integrated areas of the DNP-enhanced NMR signal \( A_{DNP} \) with the area of the equilibrium NMR signal \( A_{eq} \) detected in the 99.2\% \( ^{29}\text{Si} \)
sample after 10–24 h of magnetization in the magnetic field of 7 T at 300 K. We employed relations

$$E = \frac{A_{DNP}}{A_{eq}} \cdot \frac{T}{300[K]} \cdot \frac{7[T]}{B_{sat}},$$

and

$$P_N = E P_{N0} = E \tanh \left( \frac{h \gamma N B}{2kT} \right),$$

where $T$ and $B$ are the temperature and the magnetic field used for saturation in the EPR spectrometer, respectively, $h$ is Planck’s constant, $k$ is Boltzmann’s constant, and $\gamma_N$ is the $^{29}$Si gyromagnetic ratio. The equilibrium nuclear polarization degree is $P_{N0} = 4.8 \times 10^{-4}$ at $B = 7$ T and $T = 300$ K.

The equilibrium NMR signals were strong in the 99.2% $^{29}$Si sample, while they were weak for samples with $^{29}$Si isotope $f_{29Si} < 4.7\%$. Therefore, values of $P_N$ and $E$ for low $^{29}$Si samples were obtained by using $A_{eq}$ values with respect to the 99.2% Si sample, taking into account the difference in the isotopic content. We used the ratio of the integrated NMR signals $A_{DNP}/A_{eq}$ rather than signal amplitudes ratio because of the dependence of the NMR line shape and linewidth on the $^{29}$Si isotope amount.24,61

An exponential increase of nuclear polarization with saturation time $t$ was observed in all the investigated samples. The steady-state values of the DNP enhancement, $E^{ss}$, DNP degree, $P_{N}^{ss}$, and nuclear polarization time $T_{1N}^{ss}$, were determined using the fitting the exponential growth of the DNP NMR signal with the time. In the case of illumination with the 100-W incandescent halogen lamp, the nuclear polarization time $T_{1N}^{ss}$ was in the range of 90–180 min, whereas under laser illumination the time was shorter, about 50–80 min, depending of the samples. It is found that the DNP process and values of $E^{ss}$ and $P_{N}^{ss}$ are the same between the halogen and laser excitations. The only difference appears in the nuclear polarization time $T_{1N}^{ss}$, where the laser excitation is much shorter than that with the halogen lamp. At low temperatures (3.1–20 K), the equilibrium NMR signals cannot be observed because of extremely long nuclear spin-lattice relaxation time without illumination.

### III. RESULTS AND DISCUSSION

The efficiency of the $^{29}$Si DNP using the photoexcited triplet centers depends on a number of conditions: the concentrations of spin-triplet centers and $^{29}$Si isotopes, the electron spin polarization, lifetime, and spin-lattice relaxation time of the triplet centers. The $^{29}$Si nuclear spin polarization induced around the Si-SL1 centers expands to the whole sample by nuclear spin diffusion. For DNP via phosphorus in silicon, the $^{29}$Si nuclear spin diffusion is relatively fast even for $<4.7\%$ $^{29}$Si crystals, and it is the rate of DNP around the paramagnetic centers that limits the overall DNP rate. The additional obstacle associated with DNP via phosphorus donors is the existence of the diffusion barriers, whereas such barriers disappear around SL1 upon relaxation to the ground singlet state. Therefore, the purpose of this section is to show the important features that eventually lead to optimization of the DNP condition to achieve the high $^{29}$Si nuclear polarization.

![FIG. 1. EPR spectra detected under band-gap illumination in 1-MeV electron irradiated naturally and abounded (4.7\% $^{29}$Si) n-Si for $B || (110)$ (spectrum a) and $B || (111)$ (spectrum b). Weak lines at $B \approx 280$ and 366 mT (indicated by arrows in the spectrum b) correspond to the Si-PT1 EPR signals of the excited triplet states of $(C_{3}-Si-C_{3})^{b}$ centers (Refs. 54 and 65).](https://example.com/physrevb_075201/fig1.png)

**A. Photoexcited triplet states of oxygen + vacancy complexes in $^{29}$Si isotope-controlled silicon**

Without illumination, no EPR signal was observed in all the samples since the Fermi level is near the middle of forbidden gap and all radiation defects are not paramagnetic after the high dose of irradiation. Under or after the band-gap illumination, several overlapping weak EPR peaks of paramagnetic centers having spin $S = 1/2$ were observed. Such peaks included EPR of neutral phosphorus donors, negatively charged A-centers, and divacancies. An estimated total concentration of these light-induced paramagnetic centers was below $10^{15}$ cm$^{-3}$. A strong Si-SL1 signal emerged under steady-state illumination, as shown in Fig. 1. The lines labeled as A, B, C, D, and several weak lines at magnetic fields 320–330 mT originate from the excited triplet states of the neutral A-center.30 The lines A and B of the Si-SL1 spectrum having the signs opposite to C and D correspond to emission of the microwave power, which shows that there is nonequilibrium distribution of populations between the $| +1 \rangle$ and $| 0 \rangle$ and between $| 0 \rangle$ and $| -1 \rangle$ states. In addition, the electron spin-lattice relaxation time $T_{1S}$ is longer than the lifetime of the photoexcited triplet centers. The electron spin polarizations $P_{e}(+1,0)$ and $P_{e}(0,-1)$ between these sublevels are opposite

$$P_{e}(+1,0) = -P_{e}(0,-1) \gg P_{o},$$

where $P_{o}$ is the Boltzmann equilibrium polarization.

The spin Hamiltonian for spin $S = 1$ centers interacting with nuclear spin $I$ in magnetic field $B$ can be written as

$$H = \beta g_S B S + S A I + \beta_N g_N B I.$$
The principal values of $D$, $S$, and $A$ tensors determined in Ref. 50 are shown in Fig. 2.

$E = (D_{xx} - D_{yy})/2$ are needed to describe the fine structure of the spin $S = 1$ EPR spectra. The third term in Eq. (4) corresponds to the hf interactions between electron and nuclear spins with the $A$ tensor that includes both the isotropic contact and anisotropic dipole-dipole interactions.

The Si-SL1 spectrum exhibits the orthorhombic symmetry. The principal values of $g$, $D$, and $A$ tensors were determined in Ref. 50. The maximum splitting $\Delta B \approx 65.7 \times 10^{-4}$ cm$^{-1}$ and antiferromagnetic sublevels with spin projections $m_s = \pm 1$ and $m_s = 0$ at $B_{ac} = \Delta B/2 \approx 35$ mT for $B || (110)$. As shown in Fig. 1(b), for $B || (111)$ all EPR lines are grouped near magnetic fields about 305 and 340 mT. The energy levels of the Si-SL1 center calculated for $B || (110)$ using spin Hamiltonian parameters determined in Ref. 50 are shown in Fig. 2.

The structure of the O-V center is well established; an oxygen atom localized near the substitution position forms chemical bonds with two neighbor Si atoms. The remaining two dangling bonds of silicon vacancy form the bonding and antibonding molecular orbitals oriented along any of six equivalent (110) crystal axes. In the excited triplet state, two electrons with parallel spins are localized on the bonding and antibonding orbitals. The probabilities $R^+\, R^0\, R^-$ of the spin-selective transitions from the triplet to the ground singlet state are determined by spin-orbit coupling and depend, in general, on the orientation of the crystal in the magnetic field. The hf structure of the Si-SL1 EPR spectrum due to interactions between electrons and $^{29}$Si nuclei occupying the two nearest substitution positions are well resolved and shown in Fig. 3 for the samples with $f_{29Si} = 4.7$% and 99.2%.

The concentration of Si-SL1 centers has been estimated as follows. The total concentration of $A$-centers in silicon depends on the dose of irradiation and on the production rate ($\alpha \approx 0.1$ cm$^{-1}$) of $A$-centers by 1–1.5 MeV electron irradiation. With the dose of $\Phi \approx 10^{18}$ cm$^{-2}$, the concentration of $A$-centers becomes $N(A) = \alpha \Phi \approx 10^{17}$ cm$^{-3}$. What fraction of the $A$-centers is converted to SL1 centers under illumination cannot be determined directly from the EPR spectra because the line intensities depend both on the concentration and spin polarization. Therefore, the concentration of SL1 was estimated by comparing the nuclear polarization times in the phosphorus-doped samples with the known phosphorus concentration $N(P)$. Under laser photoexcitation, the nuclear polarization time $T_{1N}^0$ in the irradiated samples was $\approx 1$ h. A similar value of $T_{1N}^0 \approx 1.2$ h was observed in $n$-Si containing $N(P) \approx 5 \times 10^{16}$ cm$^{-3}$ paramagnetic phosphorus atoms. Therefore, under high-intensity illumination the concentration of the Si-SL1 centers is comparable with the total concentration of $A$-centers. It was found that amplitudes of Si-SL1 lines (A–D in Fig. 1) are approximately ten times higher than EPR lines of phosphorus atoms ($N(P) \approx 5 \times 10^{16}$ cm$^{-3}$) in the sample measured at 12 K. Taking into account the equilibrium electron polarization of phosphorus $P_{N} \approx 2$% and the number of resonance lines and their linewidths, the steady-state electron spin polarization between $|\pm 1\rangle$ and $|0\rangle$ states of SL1 centers was estimated to be about 70–80%.

### B. Optical nuclear polarization

Because DNP experiments with EPR spectroscopy are performed together with the band-gap illumination creating the triplet centers in crystals, let us first reveal the effect of illumination on nuclear spin polarization, i.e., ONP. It was shown that the doping of silicon crystals with different impurities forming deep-energy levels in the gap led to higher ONP degrees. The ONP is induced by the dipole-dipole interaction between localized electrons and distant lattice nuclei in contrast to the DNP that is driven by the contact isotropic hf interactions. The dipole-dipole part ($H_{dd}$) of hf interaction $H_{hf} = SAI$ in Eq. (4) between electrons and distant nuclei contains the spin operators $(S \pm L)$, and $(S \pm L)$, corresponding to flip-flop $(\Delta m_s = \pm 1, \Delta m_L = \mp 1)$ and $(\Delta m_s = \pm 1, \Delta m_I = \mp 1)$ and $(\Delta m_s = \pm 1, \Delta m_L = \mp 1)$.
flip-flip ($\Delta m_S = \pm 1, \Delta m_I = \pm 1$) transitions, respectively, and the $(S, I \pm)$ term describing only the nuclear spin flip without electron spin transition ($\Delta m_S = 0, \Delta m_I = \pm 1$). Probabilities $w_1$, $w_2$, and $w_3$ of flip-flop, flip-flip, and nuclear spin flip transitions, respectively, are given by

\[ w_1 = \frac{1}{20} \frac{g_S^2 g_I^2 g_N^2 \beta_S^2}{r^6} \frac{1}{1 + (\omega_S - \omega_I)^2 \tau_c^2}. \]  

\[ w_2 = \frac{6}{20} \frac{g_S^2 g_I^2 g_N^2 \beta_S^2}{r^6} \frac{1}{1 + (\omega_S + \omega_I)^2 \tau_c^2}. \]  

\[ w_3 = \frac{3}{20} \frac{g_S^2 g_I^2 g_N^2 \beta_S^2}{r^6} \frac{\tau_c}{1 + \omega_I^2 \tau_c^2}. \]

where $\omega_S$ and $\omega_I$ are the electron and nuclear Zeeman frequencies in magnetic field $B$, respectively, $\tau_c$ is the correlation time of the fluctuating electron-nuclear hf interaction. The correlation time for photoexcited triplet centers is determined by random changes of electron spin projections caused by the spin-lattice relaxation with the rate $1/T_1S$ and by the recombination rate of triplet centers $1/\tau_T$, where $\tau_T$ is their lifetime.

\[ \frac{1}{\tau_T} = \frac{1}{T_1S} + \frac{1}{\tau_c}. \]  

The inversions of some EPR lines of the photoexcited triplet states [see the lines A, B, C, and D in Fig. 1(a)] show that the electron spin-lattice relaxation time is longer than the lifetime, $T_1S \gg \tau_T$. For Si-SL1 centers, the lifetime $\tau_T \approx 10^{-3}$ s and spin-lattice relaxation time $T_1S > 0.1$ s at $T < 12$ K were reported.\(^{63}\) The probabilities of the transitions, Eqs. (5)–(7), depend on the magnetic field $B$ and on the correlation time $\tau_c$. Flip-flop ($w_1$) and flip-flip ($w_2$) transitions are important only in the weak magnetic fields $B \ll (\gamma_I \tau_c)^{-1}$, while the nuclear relaxation probability $w_3$ is significant in the larger magnetic fields up to $B \approx (\gamma_I \tau_c)^{-1}$. These transitions are responsible for the ONP carried out in weak magnetic fields without microwave saturation of EPR lines.\(^{64,65}\)

In general, the deviation of nuclear polarization degree $P_N$ from its equilibrium value $P_{N0}$ is given by

\[ P_N - P_{N0} = -w f_s (P_e - P_{e0}). \]  

where

\[ w = \frac{w_2 - w_1}{w_1 + 2w_3 + w_2}. \]  

Here $f_s \leq 1$ is a factor describing the decrease of the nuclear polarization degree due to relaxation caused by extraneous paramagnetic centers and is given by $f_s = 1/(1 + f)$, where $f$ is the well-established leakage factor discussed in detail in Ref. 44. The electron polarization of the photoexcited triplet centers $P_{eT}$ is determined as

\[ P_{eT} = \frac{N^+ - N^-}{N^+ + N^- + N^0 + N^-}. \]

where $N^+$, $N^0$, and $N^-$ are the populations of the $|+1\rangle$, $|0\rangle$ and $|-1\rangle$ states, respectively. At $B \gg B_{ac}$, $P_{eT}$ is zero because of the equal populations of the $|+1\rangle$ and $|-1\rangle$ states. At lower magnetic fields, $B \sim B_{ac}$, electron polarization $P_{eT} \neq 0$ is opposite to equilibrium Boltzmann polarization because of the mixing of states with different spin projections.\(^{65}\)

The maximum values of $P_{eT}$ and, consequently, $P_N$, are achieved at $B = B_{ac}$.

Figure 4 shows the dependences of the $^{29}$Si NMR signal intensity on the magnetic field, observed after band-gap illumination of the electron irradiated $n$-Si ($N(P) \approx 5 \times 10^{16}$ cm$^{-3}$) (o: curve 1) and the high-resistance ($\sim 1000$ $\Omega$ cm) $p$-type Si (●: curve 2) with the natural abundance (4.7%) of the $^{29}$Si isotope after 15 min of illumination by the 100-mW halogen lamp at $T = 8$ K and $B$ ($\|$) (111). Curve 3 is the calculated dependence of $P_N$ on $B$ normalized by the maximal value at $B = B_{ac}$. Curve 4 shows the dependence of the equilibrium $^{29}$Si NMR signal on $B$. Hereafter, the positive and negative signs of NMR signals correspond to DNP in opposite and the same directions with respect to equilibrium nuclear polarization, respectively.

The enhancement of ONP-NMR signals extrapolated to the infinite time of illumination at $B = 35$ mT and $T = 8$ K is $E^{29} \approx 520$. However, the effect of ONP in the following DNP experiments is negligible since they will be performed at a higher magnetic, $B \sim 300 - 360$ mT.

### C. Dynamic nuclear polarization

Figure 5 shows the $^{29}$Si NMR signals observed after a 10-min saturation at the magnetic fields corresponding to the maxima of the Si-SL1 EPR line. Here, significantly stronger NMR signals exceeding $10^3$ to $10^4$ times the equilibrium NMR...
signals were observed. Similar DNP enhancements of the NMR signal were observed for saturation of other Si-SL1 EPR lines, indicating that each EPR transition involves a strong nonequilibrium electron polarization. In contrast to ONP, where nuclear polarization is due to the difference in the relaxation with the probabilities given by Eqs. (5)–(7), DNP is driven by the flip-flop and flip-flip transitions between the electron and 29Si nuclear spins that are induced by the resonance microwave field, with the frequency tuned specifically to each transition. To reveal the DNP mechanism, the orientation of 29Si was obtained by saturation of the EPR transitions of Si-SL1 centers at different magnetic fields, B_{sat}, using the EPR spectrometer, and the resulting polarization of 29Si was determined by NMR by comparing the first-derivative EPR line shape. Figure 6 shows that the DNP of 29Si nuclei is a result of solid-effect43–45 due to saturation of the forbidden flip-flop and flip-flip transitions corresponding to the electron and distant 29Si nuclear spin flips in the opposite and in the same directions, respectively. The shift, ΔB_{±}, of the forbidden flip-flop and flip-flip transitions from the center of the EPR line at B_0 ≃ 357.5 mT is equal to ΔB_{±} = B - B_0 = ±B_{sat}(γ_e/γ_n) = ±0.11 mT for 29Si nuclei.

As can be seen from Fig. 6(a), the value of ΔB exceeds the peak-to-peak linewidth (PPLLW) of the Si-SL1 EPR signal in the 0.59% 29Si sample. Two peaks of 29Si DNP at ΔB_{±} ≃ ±0.11 mT corresponding to the flip-flop and flip-flip transitions lead to the opposite signs of nuclear polarization. This is a good example of the so-called resolved solid-effect.43–45 As can be seen from Fig. 6(a), the regions of magnetic fields where DNP arises under microwave saturation of the flip-flop and flip-flip transitions exceed the PPLLW of the EPR line. Furthermore, these ranges are shifted slightly from the exact positions of the flip-flop and flip-flip transitions marked by arrows toward the central line. This can be explained by a small contribution of dipole-dipole interactions between electron and distant nuclear spins. In the 4.7% 29Si sample [Fig. 6(b)], the PPLLW is comparable with the splitting between the forbidden flip-flop and flip-flip transitions, and DNP is therefore due to partly resolved solid-effects. The satellites observed near the EPR line at ±0.35 and ±0.1 mT are caused by hf interaction with more distant nuclei occupying the places in the second and third lattice shells of the A-center, respectively. The hf interaction with more distant nuclei is weaker, gives the contribution to the EPR linewidth, and is responsible for the DNP expansion across the sample by the nuclear spin diffusion process. The EPR lines of the Si-SL1 spectrum in the 99% 29Si sample [see Fig. 6(c)] are broadened by dipole-dipole interaction with the 29Si lattice nuclei. The PPLLW exceeds the value 2ΔB_{±} ≃ ±0.22 mT, and the shape of P_{ONP} dependence on B_{sat} resembles the shape of the first derivative of the EPR line. This indicates that DNP is a result of differential solid-effect.44 Here, the microwave field saturates the forbidden flip-flop and flip-flip transitions of different spin packets at the same time to result in significantly fewer polarization degrees of 29Si.
The DNP degree $P_N$ increases exponentially in time $t$ and approaches its steady-state value $P_{ss}^N$. It was found that the nuclear polarization rate $1/T_{1N}^p$, determined by exponential fit of the experimental dependences of $P_N$ on $t$, increases with the light intensity that produces higher concentrations of the triplet centers. The intensity of Si-SL1 EPR lines and $P_N$ are in accordance with this picture for the temperature range 4–20 K but decreases at higher temperatures in accordance with our earlier investigations.\(^4\) Such a decrease of $P_N$ at $T > 20$ K is explained by the decrease in electron spin-lattice relaxation, which, in turn, decreases the electron spin polarization degree between magnetic sublevels of Si-SL1 centers.\(^40,61\)

To achieve the higher DNP degree in shorter time, we used the laser excitation at the light power up to 700 mW. To prevent the heating of samples by high light intensity, the experiments were performed at temperatures 3.1–3.2 K that were realized by the direct contact with the pumped liquid helium. The results are summarized in Table I. Here, the electron spin polarization between the magnetic sublevels of the triplet center was estimated (see Sec. III A) as $P_e \approx 70–80\%$. The DNP degree obtained by saturation of the flip-flop or flip-flip transitions of only one of the 12 available EPR lines of Si-SL1 already led to a very impressive $6.4\%$, which is large enough to implement the efficient algorithmic cooling protocol\(^28\) to increase the polarization further for initialization. This $6.4\%$, however, is still limited by the extraneous nuclear relaxation caused by paramagnetic centers that do not participate in the DNP process because the A-centers are oriented in the Si lattice along six equivalent $\langle 110 \rangle$ axes. Due to this symmetry, Si-SL1 centers yield 12 EPR lines. Therefore, DNP with $B \parallel \langle 110 \rangle$ uses only one of 12 EPR transitions, and the remaining 11 transitions can be considered as paramagnetic centers, leading to suppression of the DNP degree with the factor $f_{\alpha} = 1/12 \approx 0.083$. The six-time increase of the DNP degree is expected for the orientation $B \parallel \langle 111 \rangle$ by saturating simultaneously all the Si-SL1 EPR lines that group together around the same magnetic field [see Fig. 1(b)]. Figure 7 shows results of a proof-of-concept experiment to demonstrate nearly a sixfold increase in DNP degrees, 0.17 to 0.97 as listed in Table I, for $B \parallel \langle 111 \rangle$, with respect to that in $B \parallel \langle 110 \rangle$ in the 99.2% isotopically enriched Si sample. The Si-SL1 EPR lines in this sample are broadened by hf interaction overlap very well [Fig. 3(c)], i.e., and simultaneous excitations of different lines are possible with an expense of overall fewer DNP degrees due to the differential solid effect. However, Si-SL1 EPR lines in the 29Si <4.7% samples are very narrow [Fig. 1(b)], and it is possible to adjust the angle and magnetic field since only two or three Si-SL1 EPR lines overlap. In such experiments approximately a two- or three-time increase of DNP NMR signals was detected. Unfortunately, it is difficult to reproduce exactly the same sample position (orientation) in the EPR spectrometer after the measurement of the NMR signal to determine the steady-state DNP degree. The estimated steady-state DNP degrees $P_{ss}^N$ for naturally abounded irradiated Si sample are listed in the Table I (column 5). In the future, if all of the 12 transitions could be saturated by applying 12 microwave resonance frequencies simultaneously, the nuclear polarization degree would be $6.4\% \times 12 = 76.8\%$, which is approximately equal to the estimated electron spin polarization. Therefore, the electron polarization of the SL1, in principle, is being transferred to the nearest-neighbor 29Si nuclear system very efficiently without much loss.

In addition, EPR lines corresponding to the forbidden $\Delta m_S = \pm 2$ transition were observed in all samples at $B \approx 160$ mT. These lines have a weak angular dependence, and all lines overlap well regardless of the 29Si abundance. The total electron spin polarization at $B \approx 160$ mT is also not equal to Boltzmann polarization because of the mixing of $|+1\rangle$, $|0\rangle$, and $|-1\rangle$ states; therefore, the DNP can be realized by saturation of the flip-flop and flip-flip electron-nuclear transitions. However, DNP obtained by saturation of the $\Delta m_S = \pm 2$ line of natural silicon reached $P_{ss}^N \approx 0.56\%$ only with the nuclear polarization time $T_{1N}^p \approx 61$ min.

### D. DNP by saturation of the Si-SL1 hf lines

It was found that DNP could be realized by microwave excitation of electron-nuclear transitions not only within the central Si-SL1 EPR lines but also by excitation of satellites arising from hf interactions between the SL1 electron and the nearest 29Si nuclear spins. Figure 8 shows the dependence of

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**TABLE I. Summary of DNP experiments performed at 3.1 to 3.2 K.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>DNP</th>
<th>$T_{1N}^P$ min</th>
<th>$B \parallel \langle 110 \rangle$</th>
<th>$B \parallel \langle 111 \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.59% 29Si</td>
<td>RSE</td>
<td>75</td>
<td>6.41</td>
<td>–</td>
</tr>
<tr>
<td>4.7% 29Si</td>
<td>PRSE</td>
<td>72</td>
<td>6.37</td>
<td>(9–11)(^4)</td>
</tr>
<tr>
<td>99.2% 29Si</td>
<td>DSE</td>
<td>59</td>
<td>0.17</td>
<td>0.97</td>
</tr>
</tbody>
</table>

\(^4\)An estimated steady-state DNP degree for $B \parallel \langle 111 \rangle$ when simultaneous saturation of two completely overlapping Si-SL1 lines is realized experimentally.

\(^b\)An estimated steady-state DNP degree for $B \parallel \langle 111 \rangle$ when simultaneous saturation of three completely overlapping Si-SL1 lines is realized experimentally.
The hf interaction with the nearest 29Si nuclei splits the electron Zeeman splitting corresponding to the transitions between the SL1 electron and the nearest-neighbor 29Si nuclear spins. The EPR lines marked by arrows are satellites due to the hf interaction between the SL1 electron and distant 29Si nuclear spin system. Let us consider an EPR transition between \( |+\rangle \) and \( |0\rangle \) spin states of Si-SL1 center (a), hf splitting due to interaction between electron and nearest nuclear spin (b), nuclear Zeeman splitting by distant 29Si nuclei (c), and possible transitions between energy levels induced by microwave field (d) and (e).

By considering the simple energy level diagram (not in scale) showing the electron Zeeman splitting between \(|+\rangle\) and \(|0\rangle\) spin states of Si-SL1 center (a), hf splitting due to interaction between electron and nearest nuclear spin (b), nuclear Zeeman splitting by distant 29Si nuclei (c), and possible transitions between energy levels induced by microwave field (d) and (e).

The weak hf interactions between these nuclei and electron spins, the splitting of \( m_S = \pm 1/2 \) is equal to the nuclear Zeeman frequency. The flip-flop and flip-flip transitions leading to DNP of the second-nearest-neighbor 29Si are shown by arrows in Figs. 9(d) and 9(e). Here, the flip-flip transitions between electron and distant nuclear spins \(|+1, +1/2, +1/2\rangle \leftrightarrow |0, +1/2, -1/2\rangle \) [Fig. 9(d)] correspond to the high-field hf line [see Fig. 8(a)], and additional flip-flip transitions exist as for the nearest-neighbor nuclei \(|+1, +1/2, +1/2\rangle \leftrightarrow |0, -1/2, +1/2\rangle \) and \(|+1, +1/2, -1/2\rangle \leftrightarrow |0, -1/2, -1/2\rangle \). For the low-field hf line, the additional flip-flip transitions correspond to \(|+1, -1/2, +1/2\rangle \leftrightarrow |0, +1/2, +1/2\rangle \) and \(|+1, -1/2, -1/2\rangle \leftrightarrow |0, +1/2, -1/2\rangle \). These additional transitions (W) lead to the spin polarization of nearest-neighbor nuclei in the manner more negative for the low-field hf line and more positive for the high-field hf line, as seen in Fig. 8.

E. Impact of the present study on silicon quantum information processing

Because the lifetime of the triplet states (SL1) of O-V centers is only a few milliseconds, it is not practical to employ the spin-triplet state of SL1 as a qubit or quqtrit in which three levels are used for quantum information processing. However, taking advantage of this short lifetime, SL1 can be regarded as an on-demand qubit manipulator by controlling the timing of light illumination to form SL1. Otherwise, it stays in the singlet ground state of an O-V center, which is nonparamagnetic, i.e., it is immune from decohering nearby working qubits. Consequently, there are two ways of implementing SL1 centers for silicon-based quantum information processing: (i) as a quantum information input source and

FIG. 8. The dependences of the 29Si DNP NMR signal amplitude on the magnetic field \( B_{\text{ind}}(\bullet) \) for \( B \parallel (110) \) and \( B_0 = 359.7 \text{ mT} \) and the first derivative of the Si-SL1 EPR lines (solid curves) corresponding to the transitions between \(|+1\rangle\) and \(|0\rangle\) states for the 4.7% (a) and 99.2% 29Si (b) samples. The EPR lines marked by arrows are satellites due to the hf interaction between the SL1 electron and the nearest-neighbor 29Si nuclear spins.

FIG. 9. Energy level diagram (not in scale) showing the electron Zeeman splitting between \(|+\rangle\) and \(|0\rangle\) spin states of Si-SL1 center (a), hf splitting due to interaction between electron and nearest nuclear spin (b), nuclear Zeeman splitting by distant 29Si nuclei (c), and possible transitions between energy levels induced by microwave field (d) and (e).
readout node of the nearby $^{29}\text{Si}$ nuclear spin qubits, as already shown in Ref. 27, and (ii) as a $^{28}\text{Si}$ nuclear spin polarizer in order to reduce the magnetic fluctuation in silicon to protect other qubits from decoherence. The present study sheds light on the latter issue (ii). Currently, phosphorus$^{12,13,21-23}$ and bismuth$^{26}$ donors and gate-defined quantum dots$^{14}$ are the most experimentally advanced qubits in silicon. For implementation of such qubits, isotopically enriched $^{28}\text{Si}$ or $^{30}\text{Si}$ single crystals that are depleted of the background $^{29}\text{Si}$ nuclear spins are preferred since the magnetic field fluctuation arising from flip-flops among $^{29}\text{Si}$ nuclear spins serves as a source of decoherence. However, one can employ naturally available silicon with 4.7% $^{29}\text{Si}$ if the majority of background $^{29}\text{Si}$ nuclear spins can be polarized to suppress the flip-flops. For such purposes, Si-SL1 centers are ideal since, as shown in the present study, it is feasible in the future to achieve up to $\sim 77\%$ of the $^{29}\text{Si}$ polarization spanning the entire silicon sample by saturating the spin-triplet levels of SL1. Moreover, after achieving the needed polarization, termination of the light illumination causes Si-SL1 decays to O-V singlet states in a few milliseconds to become ineffective decoherence sources for working qubits. An additional advantage of the present scheme is that it can be applied in both $n$-type and $p$-type silicon. The process to introduce O-V centers throughout the sample is rather straightforward. One can take commercially available Czochralski silicon, which typically contains $10^{18}$ cm$^{-3}$ of oxygen, and gamma irradiate it with a simple cobalt source or the like.

IV. CONCLUSIONS

The photoexcited spin $S = 1$ states (Si-SL1 centers) of the oxygen + vacancy complexes (A-centers) have been employed for DNP of $^{29}\text{Si}$ nuclei. The steady-state electron spin polarization between the triplet spin states $|\pm 1\rangle$ and $|0\rangle$ was found to be 70–80%, and such high electron polarization was transferred successfully to the lattice $^{29}\text{Si}$ nuclei by solid-effect using the microwave saturation of the electron-nuclear flip-flop and flip-flip transitions. The $^{28}\text{Si}$ DNP degree $\sim 6.4\%$ was achieved after 2 to 3 h of saturation of only one of 12 Si-SL1 EPR lines. The remaining 11 EPR transitions of Si-SL1 centers lead to extraneous nuclear relaxation, limiting DNP degree with factor $f_n$ about 0.083. It was shown that the efficiency of DNP can be increased by saturation of several EPR lines. In 99.2% $^{29}\text{Si}$ isotope-enriched sample the saturation of the EPR lines of Si-SL1 centers with magnetic field $\mathbf{B} \parallel (111)$ leads to the six times higher DNP degree when the EPR lines overlap completely. It was demonstrated in silicon with $^{29}\text{Si}$ isotope abundance $\leq 4.7\%$ that the simultaneous saturation of two (or three) EPR lines increases the DNP degree two (or three) times.

The present systematic study has shown that optical polarization of the $^{29}\text{Si}$ nuclei is effective only in weak magnetic fields $B < 100$ mT, and contribution of this optical orientation is negligibly small in the DNP process. The transformation of the DNP mechanisms from the resolved to differential solid-effect was found with the increasing abundance of $^{29}\text{Si}$. DNP was observed not only under saturation of the electron-nuclear flip-flop and flip-flip transitions but also by saturation of the hf satellite EPR transitions arising from the interactions with the nearest $^{29}\text{Si}$ nuclei. Asymmetries in the DNP line shape were observed due to additional flip-flop and flip-flip transitions between SL1 electrons and nearest-neighbor $^{29}\text{Si}$ nuclear spins.

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