Microscopic control of $^{29} \text{Si}$ nuclear spins near phosphorus donors in silicon

J. Järvinen,1,∗ D. Zvezdov,1,2 J. Ahokas,1 S. Shelyudyakov,1 O. Vainio,1 L. Lehtonen,1 S. Vasiliev,1 Y. Fujii,3 S. Mitsudo,3 T. Mizusaki,3 M. Gwak,4 SangGap Lee,4 Soonchil Lee,5 and L. Vlasenko6

1Wihuri Physical Laboratory, Department of Physics and Astronomy, University of Turku, 20014 Turku, Finland
2Institute of Physics, Kazan Federal University, Russia
3Research Center for Development of Fourier-Infrared Region, University of Fukui, 3-9-1 Bunkyo, Fukui 910-8507, Japan
4Division of Materials Science, Korea Basic Science Institute, 169-148 Gwahak-ro, Yuseong-gu, Daejeon 305-806, Korea
5Department of Physics, Korea Advanced Institute of Science and Technology, 291 Daehak-ro, Yuseong-gu, Daejeon 305-701, Korea
6A. F. Ioffe Physico-Technical Institute, Russian Academy of Sciences, 194021 St. Petersburg, Russia

(Dated: November 12, 2014)

We demonstrate efficient control of spin orientation of $^{29} \text{Si}$ nuclei for specific lattice sites near $^{31} \text{P}$ donors in silicon crystals. High resolution magnetic resonance experiments were performed at low (100-500 mK) temperatures and in high magnetic field of 4.6 T. We found that excitation of the double electron-nuclear transitions leads via the resolved solid effect to a pattern of narrow holes and peaks in the ESR lines of $^{31} \text{P}$. The patterns coincide well with the predictions based on the known superhyperfine interaction of $^{29} \text{Si}$ with $^{31} \text{P}$ electron. This method can be used for initialization of qubits based on $^{29} \text{Si}$ nuclear spins in the idea of all-silicon quantum computer. A similar control of the $^{29} \text{Si}$ via the Overhauser effect did not produce patterns but a very narrow hole of only 15 mG wide in the ESR line. This is explained by the spin diffusion during the microwave pumping.

Nuclear spins are among the best candidates for qubits of a quantum computer (QC). Long coherence times and well known magnetic resonance techniques for control and read out of the spin state are the main arguments behind the Kanes suggestion of utilizing electron and nuclear spins of phosphorus donors in silicon (Si:P) for this purpose. However, practical realization of this idea meets with the difficulties of manufacturing complicated nanostructures, manipulation and detection of a single spin. Another approach relies on the idea of utilizing large ensembles of identical spins which operate coherently, which greatly enhances the net response of the spin system. Thus a successful 12 qubit operations were realized using nuclear magnetic resonance (NMR) of molecules in liquids. Different spins inside molecules are addressed because of tiny differences in their resonance frequencies caused by the chemical shifts. A similar approach, also based on large spin ensembles, utilizes spectral holes in inhomogeneously broadened spectral lines. In this case spectrally resolved spin packets with different resonance frequencies are selectively addressed.

Spin dynamics of $^{31} \text{P}$ donors in silicon is strongly influenced by the spin-1/2 $^{29} \text{Si}$ nuclei located inside the relatively disperse 2 nm electron cloud of the donor. For normal isotopic composition (4.7 % of $^{29} \text{Si}$) there are about 70 such nuclei inside the electron cloud. Interactions of $^{31} \text{P}$ electron with them leads to a loss of coherence of the electron spin. Therefore, the presence of $^{29} \text{Si}$ nuclei was considered as a nuisance and substantial research efforts were directed onto the studies of isotopically purified silicon crystals. However, the spins of $^{29} \text{Si}$ nuclei can be also used as qubits. Having several $^{29} \text{Si}$ nuclei with different frequency shifts due to interactions with the donor electron, creates a possibility of addressing them selectively by RF excitation. The number of such qubits is defined by the amount of spectrally resolved positions of $^{29} \text{Si}$ nuclei inside the donor electron cloud and may exceed several tens. One may utilize ensembles of these qubits for building all-silicon solid state QC in a similar fashion as it was done with the nuclei of molecules in the liquid state NMR QC.

In this work we demonstrate a simple and efficient way of manipulating nuclear spins of $^{29} \text{Si}$ located in specific lattice sites near $^{31} \text{P}$ donors. We utilize a method of dynamic nuclear polarization (DNP) based on partial saturation of forbidden double electron-nuclear transitions, the so-called Solid Effect (SE), for preparation of identical spin states in large ensembles of donors. In our attempts of using other DNP method, the Overhauser Effect (OE), we saturated allowed ESR transitions in a narrow regions of inhomogeneously broadened lines. This has led to emergence of narrow spectral "holes" and other peculiar features in the ESR line shape not observed before and related with nuclear polarization of $^{29} \text{Si}$. The polarized states of $^{29} \text{Si}$ survived for many hours. We explain such long life times by locking the spin inside a spin diffusion barrier caused by the dipolar fields of the electron spins of donors.

We used a sample of phosphorus doped ($n(P) \approx 6.5 \times 10^{16} \, \text{cm}^{-3}$) natural silicon (4.6 % $^{29} \text{Si}$) cut to a $2 \times 2 \times 20 \, \text{mm}$ thick and $70 \, \mu \text{m}$ thick square with the $(111)$ crystal axis perpendicular to the sample surface and parallel to the static magnetic field. The sample was glued on the flat mirror of an open Fabry-Perot cavity of a cryogenic heterodyne EPR spectrometer operating at frequency of 128 GHz and in static magnetic field.
of 4.6 T. The spectrometer ensures high enough sensitivity without field or frequency modulation, using a high quality synthesized mm-wave source $^{11}$. To avoid saturation effects for detection of ESR spectrum we used very small excitation powers of the order of several pW. Pumping the ESR transitions in DNP and hole burning experiments was performed at highest available excitation power of 400 nW. Sample cell was cooled to temperatures 0.1-3 K by a dilution refrigerator.

The well known ESR spectrum of $^{31}$P in silicon consist of two lines, separated by 42 G due to hyperfine interaction of donor electron with its own nucleus. The hyperfine level diagram for the system of $^{31}$P electron interacting with its own nucleus is shown with thick lines in Fig. 1A. The superhyperfine interaction with a single $^{29}$Si nucleus leads to a further level splitting, which is shown schematically Fig. 1B. Interaction of the electron with many $^{29}$Si nuclei leads to inhomogeneous broadening of the $^{31}$P ESR line. When the $^{29}$Si spins are unpolarized the ESR linewidth is about 4 G. We note that the spin polarization of the $^{29}$Si energy levels is opposite to $^{31}$P levels due to the negative gyromagnetic factor of $^{29}$Si.

Manipulation of nuclear spins can be performed by the well known methods of Dynamic Nuclear Polarization (DNP), utilizing the Overhauser (OE) and Solid (SE) effects. In the OE DNP the allowed ESR transitions are saturated, which is followed by the thermal relaxation via the forbidden transitions involving simultaneous spin flips of electron and nucleus. In the SE the forbidden transitions are excited with high RF power followed by the spin relaxation via the allowed transitions. In strong magnetic field of 4.6 T used in this work the forbidden transitions are well separated from the allowed ones as shown in Fig. 1B. Thus the above mentioned DNP methods can be performed independently, and one may realize resolved OE and SE. In this work we shall consider transitions for the $^{29}$Si:P system which involves changes of the electron spin of the donor and nuclear spin of $^{29}$Si locating nearby. The spin of the donors own nucleus remains unchanged. To avoid confusion we denote spin wave functions for the three spins as $|\uparrow\uparrow\downarrow\rangle$ with the arrows pointing the electron, $^{31}$P, and $^{28}$Si spin directions with respect to magnetic field which is directed upwards (see the diagram in Fig. 1A).

We performed SE DNP on the $^{29}$Si:P by pumping one of the four forbidden transitions locating at $\pm 13.9(1)$ G outside the both ESR lines of $^{31}$P (dotted lines in fig. 1B) with maximum available RF power. The forbidden transitions are too weak to be detected directly with our spectrometer, but the result of the pumping can be well seen in the ESR line. In fig. 2A, the low field line is shown after pumping the $|\downarrow\uparrow\downarrow\uparrow\rangle \rightarrow |\uparrow\uparrow\downarrow\rangle$ transition at temperature of 200 mK for 36 min. Subtracting the undisturbed ESR line background reveals the anti-symmetric pattern of peaks (on the left) and holes (on the right) that appeared as a result of the pumping. A similar experiment performed on the other $|\downarrow\uparrow\downarrow\rangle \rightarrow |\uparrow\uparrow\uparrow\rangle$ transition located at -13.9 G from the low field line, created a pattern which is opposite to the previous result. In Fig. 2B, we present both of the patterns obtained after 200 signal averages for improving the signal-to-noise. The patterns remained unchanged for very long time at temperatures below 0.5 K. We were able to study them for many hours without any significant change. Similar results were also obtained after pumping forbidden transitions near the high field line of $^{31}$P. Appearance of the pattern, as we will show below, is caused by the DNP of $^{28}$Si in certain lattice sites. This is a new and impressive feature of the resolved SE, especially taking into account the relatively weak saturation of the forbidden transitions with the very small ESR power (400 nW) available.

For an explanation of the observed patterns we consider a donor electron spin interacting with N $^{28}$Si nuclei. Energy levels can be found using the following Hamiltonian

$$H = -g_{e}\mu_{B}B_{0}S_{z} + \sum_{k=1}^{N}(-g_{n}\mu_{n}B_{0}I_{z,k} - a_{k}S_{z}I_{z,k} + S_{T\cdot k}I_{k}).$$

(1)

Here $g_{e} = -1.99875$ and $g_{n} = -1.11058$ are the P elec-
is subtracted spectrum multiplied by two. (B) Solid effect DNP with solid effect. The green curve with flat background solid line with the burned hole is the spectrum just after the DNP with solid effect. The green curve with flat background.

The dashed black line is a Gaussian fit to the line. The red icon lattice occupied by $2^{9}$ fine interaction. The index $k$ labels different sites in silicon lattice site $m$. Each donor in the sample has a different number of lattice sites belonging to each line are marked.

1. The frequency is

$$ h f'_{x,l} = g_x \mu_B B_0 + g_a \mu_n B_0 - \sum_{k=1}^{N} m_k \frac{a_k}{2} - \frac{a_l}{2} \tag{3} $$

However, the difference between the forbidden and allowed transition frequencies does not depend on $x$, or on the states of the nuclei $k \neq l$ which are not involved in the transition. Indeed, we find from Eqs (2) and (3):

$$ h (f'_{x,l} - f_x) = g_a \mu_n B_0 - \frac{a_l}{2}. \tag{4} $$

The distance between the allowed and forbidden transition is solely a function of the hyperfine constant for the lattice site $l$ where the nuclear $2^{9}$Si spin is flipped. Following the spin transfer path for SE via the flip-flop transition and subsequent electron relaxation (see Fig. 1A) we expect to find a peak on the left and a hole on the right both separated from the center of the pattern by $\pm a_l/2$. For the flip-flop transition the pattern is inverted. This is in very good agreement what we see in the patterns of Fig. 2.

For calculating the intensities of the flip-flip and flip-flop transitions we use the Hamiltonian of Eq. 1. Now we cannot neglect the anisotropic hyperfine interaction as the flip-flip and flip-flop ESR transitions induced by a transversal microwave field would be completely forbidden in this case. However, we can safely neglect the off-diagonal terms of Hamiltonian connecting different $S_z$ states and direct interactions between $2^{9}$Si spins. Evaluating the transition probabilities for each lattice site $k$ we find the predictions for the SE patterns.

FIG. 2. (Color online) (A) Spectrum of the solid effect after exciting $|\downarrow\uparrow\uparrow\rangle \rightarrow |\uparrow\uparrow\downarrow\rangle$ transition at 150 mK for 36 min. The dashed black line is a Gaussian fit to the line. The red solid line with the burned hole is the spectrum just after the DNP with solid effect. The green curve with flat background is subtracted spectrum multiplied by two. (B) Solid effect ESR spectrum of transitions $|\downarrow\uparrow\uparrow\rangle \rightarrow |\uparrow\uparrow\downarrow\rangle$ (exited for 115 min) and $|\downarrow\uparrow\downarrow\rangle \rightarrow |\uparrow\uparrow\uparrow\rangle$ (exited for 140 min) plotted correspondingly with green solid and blue dashed line. The plots are averages of 200 spectra.

FIG. 3. (Color online) Spectrum of the solid effect (green) and calculated spectrum (dashed blue). The calculated relative transition probabilities are marked with the black vertical lines. The small splittings of the transitions are due to anisotropic hyperfine interaction. Above the peaks in the spectrum the coordinates of the lattice sites together with the number of lattice sites belonging to each line are marked.

$|\downarrow\uparrow\uparrow\rangle \rightarrow |\uparrow\uparrow\downarrow\rangle$ and

$|\downarrow\uparrow\downarrow\rangle \rightarrow |\uparrow\uparrow\uparrow\rangle$.
Next, we studied DNP of $^{29}$Si using the Overhauser effect. In our previous work we found that the saturation of high field line of $^{31}$P leads to a fast DNP of the donor nuclei [3]. Since now we are interested in the DNP of $^{29}$Si, the OE experiments were performed on the low field line for which the DNP of $^{31}$P is extremely slow [3].

Saturating an inhomogeneously broadened ESR line at fixed magnetic field implies that the intensity of the ESR signal is strongly reduced due to saturation. A hole appears in the line due to nonequilibrium electron spin state populations of the spin packets which are at resonance. Hole burning experiments on Si:P were previously performed [12, 13, 16] at substantially lower magnetic fields and higher temperatures. Although, several structures were observed in the spectrum, their origin remained unclear. After the excitation is reduced the electron spin states recover to equilibrium due to the spin-lattice relaxation or spin and spectral diffusion. Experiments in low fields did not provide clarification of the actual mechanisms of the hole burning and relaxation [12, 13, 16].

In this work we performed hole burning experiments with nearly monochromatic excitation source with or without small modulation of the frequency. Detection of the results of hole burning have been performed with very low excitation power without any field or frequency modulation. This allowed to resolve the resulting narrow features after pumping. Results of pumping at the center of the ESR line with the maximum excitation power for several minutes are presented in Fig. 4A. A single hole appeared in the spectrum accompanied with two narrow peaks on both sides. The observed $\approx 15$ mG width of the hole corresponds to the individual spin packet width which is given by the transversal relaxation rate of the electron spin $T_2^{-1}$ $\approx 40$ kHz. This value looks reasonable for the sample of silicon with natural abundance of $^{29}$Si [17]. Next, we repeated the pumping with frequency modulated excitation of 100 Hz rate and 100 kHz deviation. This also created a hole and a broader peak at the high field side of the hole, as is seen in Fig. 4B. In either of the cases above we have not observed any pattern of holes and peaks, contrary to the SE DNP experiments. Finally, we performed a FM pumping with the frequency deviation increased to 3 MHz. In this case, a "burnt" window as shown in Fig. 4C was created. The window was accompanied by a strong sharp peak near the right edge and much weaker peak near the left edge of the window. At temperatures below 0.5 K the results of the ESR line pumping: holes, peaks and windows faded out very slowly, with the characteristic time of several hours, much longer than the electron spin-lattice relaxation time $T_1 \approx 0.2$ s. The areas of the holes in Fig. 4A and B are approximately equal to the areas of the peaks. The shapes and the long lifetimes of the burned holes show unambiguously that the pumping of the spin packets leads, not only to their saturation, but also to redistribution of the $^{29}$Si nuclear spin orientations near the phosphorus donors.

In the explanation of the hole burning experiments we have to take into account the $^{29}$Si nuclear spin diffusion. This process proceeds with rather high rate $\gtrsim 10^{-14}$ cm$^2$/s in the bulk of silicon crystals, far away from the donors [18]. The spin diffusion is, however, strongly suppressed inside a so-called diffusion barrier which is created by the dipole fields of electron spins near the donors [19]. The size of the diffusion barrier for the samples of natural silicon is about 10 nm, which is much larger than the span of $^{31}$P electron cloud. A weak saturation of the forbidden transitions in the SE experiments does not destroy the electron spin polarization, and the spin diffusion does not influence the $^{29}$Si near the donors. Therefore, in the SE the $^{29}$Si polarization created in the specific lattice sites remains there for a very long time.

In the OE experiment, on the contrary, the allowed transitions are fully saturated and thus the electron spins are depolarized. This quenches the diffusion barrier [19] and allows rapid spreading of the $^{29}$Si polarization. Thus the OE polarization, which arise near the donors in the lattice sites where the $^{29}$Si have the strongest interaction with $^{31}$P electron, is rapidly conducted farther from the donor to the nuclei with weaker interactions. This explains why we do not observe peaks and holes corresponding to $^{29}$Si polarization in distinct lattice sites in the OE DNP experiments. Once the $^{29}$Si nuclear spin gets flipped the donor nearby gets out of resonance. Now the electron spin of this donor relaxes during a charac-

![FIG. 4. (Color online) (A) Low field ESR line of Si:P recorded before and after burning a hole. The inset shows the hole without the background signal. (B) The narrowest observed hole burned in the low field line. (C) Lineshape after applying ESR pumping with 3 MHz FM modulation at 40 nW power to the center of the low field line for 10 min.](image-url)
teristic time of $T_1 \approx 0.2 \text{ s}$ and the spin diffusion barrier starts to develop around the donor. The $^{29}\text{Si}$ polarization may propagate over a distance of few lattice constants during $T_1$ before getting frozen. Such redistribution of the $^{29}\text{Si}$ nuclear polarization under pumping may lead to appearance of sharp peaks near the burnt hole. During a window pumping the donors are not getting out of resonance, but rather remain inside the window and are re-pumped again. That is why the peaks at the sides of the window are much stronger.

Next thing to explain is why we observe a stronger peak at the high field (right) side of the burnt window. Pumping in the ESR line we excite in equal amounts the allowed $|\downarrow\uparrow\downarrow\rangle \rightarrow |\uparrow\uparrow\downarrow\rangle$ and $|\downarrow\uparrow\uparrow\rangle \rightarrow |\uparrow\uparrow\uparrow\rangle$ transitions. Since the flip-flop relaxation is usually faster than the flip-flap [20], the OE will enhance population of the $|\downarrow\uparrow\uparrow\rangle$ state. Since the $|\downarrow\uparrow\uparrow\rangle \rightarrow |\uparrow\uparrow\uparrow\rangle$ occur in higher sweep field, such re-distribution of the spin states leads to the increase of the signal on the right side from the pumping point. Evaluating the ratio of areas on the right and left sides of the pumped window in fig. 4C provides the ratio of the flip-flop relaxation rate to the flip-flap relaxation. Assuming that the $^{29}\text{Si}$ spins are unpolarized before pumping, we obtain this ratio equal to $\sim 8$.

The 15 mG width of the holes in the OE DNP corresponds to the width of the individual spin-packet, which is defined by transversal relaxation rate of donor electrons. Manipulating with $^{29}\text{Si}$ via the SE should in principle provide the same width of the holes and peaks. However, as one can see from Fig. 2, the observed $\approx 0.1$ G features are substantially broader. This extra broadening can be explained by the drift of the static magnetic field in our superconductive magnet during relatively long pumping time of tens of minutes. We believe that this effect and can be eliminated with better stabilization of the field, or if shorter pumping time can be realized by using more powerful mm-wave source. This will substantially improve the resolution and allow access to a larger number of $^{29}\text{Si}$ located in distinct lattice sites.

In a conclusion we demonstrated that the Solid Effect DNP can be used for polarization of $^{29}\text{Si}$ nuclei located in the specific lattice sites near phosphorus donors. Spin diffusion does not destroy the polarization inside the diffusion barriers around donors, which are created by the dipolar fields of the donor electron. On the contrary, in the OE DNP the diffusion barrier is quenched due to saturation of allowed electronic transitions. This leads to a rapid spread of polarization into the remote $^{29}\text{Si}$ nuclei and is seen as a narrow hole and a peak in the inhomogeneously broadened ESR line shape. The SE DNP demonstrated in our work, opens up possibilities of using ensembles of $^{29}\text{Si}$ nuclear spins for quantum information storage and processing.

---

References:

[1] B. E. Kane, Nature 393, 133 (1998)
[2] C. Negrevergne, T. Malavi, C. Ryan, M. Ditty, F. Cyr-Racine, W. Power, N. Boultant, T. Havel, D. Cory, and R. Laflamme, Phys. Rev. Lett. 96, 170501 (2006)
[3] M. S. Shahriar, P. R. Hemmer, S. Lloyd, P. S. Bhatia, and A. E. Craig, Phys. Rev. A 66, 1 (2002)
[4] S. Simmons, R. M. Brown, H. Riemann, N. V. Abrosimov, P. Becker, H.-J. Pohl, M. L. W. Thewalt, K. M. Itoh, and J. J. L. Morton, Nature 470, 69 (2011)
[5] A. M. Tyryshkin, S. Tojo, J. J. L. Morton, H. Riemann, N. V. Abrosimov, P. Becker, H.-J. Pohl, T. Schenkel, M. L. W. Thewalt, K. M. Itoh, and S. a. Lyon, Nature materials 11, 143 (2012)
[6] H. Bieh, S. Mahapatra, R. Rahman, A. Morello, and M. Y. Simmons, Nat. Commun. 4, 2017 (2013)
[7] T. Ladd, J. Goldman, F. Yamaguchi, Y. Yamamoto, E. Abe, and K. Itoh, Phys. Rev. Lett. 89, 017901 (2002)
[8] J. J. J. Pla, F. a. Mohiyaddin, K. K. Y. Tan, J. P. Debollain, R. Rahman, G. Klimeck, D. N. Jamieson, A. Dzurak, and A. Morello, (2014) arXiv:1408.1347v1
[9] J. Järvinen, D. Zvezdov, J. Ahokas, S. Sheduoyakov, O. Vainio, L. Lehtonen, S. Vasiliev, Y. Fuji, S. Mitsudo, T. Mizusaki, M. Gwak, S. Lee, S. Lee, and L. Vlasenko, (2014) arXiv:1402.4288v1
[10] S. Vasiliev, J. Järvinen, E. Tjukanoff, A. Kharitonov, and S. Jaakkola, Rev. Sci. Instrum. 75, 94 (2004)
[11] "Amplifier/Multiplier Chain (AMC) - VDI Model: WR8.0-AMC, Virginia" [12] G. Feher, Phys. Rev. 114, 1219 (1959)
[13] C. P. Poole Jr. and H. A. Barach, The theory of magnetic resonance ch. 7, 1st ed. (Wiley-Interscience, a Division of Wiley & Sons, Inc., 1972)
[14] “See suplementary material.”
[15] G. Feher and E. Gere, Phys. Rev. 114, 1245 (1959)
[16] J. R. Marko and A. Honig, Phys. Rev. B 1, 718 (1970)
[17] E. Abe, A. M. Tyryshkin, S. Tojo, J. J. L. Morton, W. M. Witzel, A. Fujimoto, J. W. Ager, E. E. Hailer, J. Isoya, S. a. Lyon, M. L. W. Thewalt, and K. M. Itoh, Phys. Rev. B 82, 121201 (2010)
[18] H. Hayashi, K. Itoh, and L. Vlasenko, Phys. Rev. B 78, 153201 (2008)
[19] G. R. Khutsishvili, Sov. Phys. Uspekhi 11, 802 (1969)
[20] C. D. Jeffries, Phys. Rev. 117, 1056 (1960)
[21] E. Hale and R. Mieher, Phys. Rev. 184, 739 (1969)
SUPPLEMENTARY MATERIAL

Transition probabilities

The Hamiltonian describing superhyperfine level splitting of an electron interacting with a $^{29}\text{Si}$ nuclei is

$$H = H_0 + H_k = -g_e\mu_B B_0 S_z - g_n\mu_B B_0 I_{z,k} - a_k S_z I_{z,k} + S \cdot T_k \cdot I_k$$

where $H_0 = -g_e\mu_B B_0 S_z - g_n\mu_B B_0 I_{z,k}$, $H_k = S \cdot T_k \cdot I_k$,

$$T_k(i,j) = \frac{\mu_0}{4\pi} g_e\mu_B g_n\mu_n \hbar^2 \left\langle \psi(r) \left| \frac{r^2\delta_{ij} - 3x_ix_j}{r^3} \right| \psi(r) \right\rangle$$

is the anisotropic superhyperfine interaction

$$a_k = \frac{2\mu_0}{3} g_e\mu_B g_n\mu_n \hbar^2 |\psi(r_k)|^2,$$

is the isotropic superhyperfine constant and $\psi$ is the electronic wavefunction. In the matrix form the spin projections are defined as

$$\psi = \begin{pmatrix} \downarrow \downarrow \downarrow \downarrow \end{pmatrix},$$

where $\downarrow$ is the electron spin and $\downarrow$ is the $^{29}\text{Si}$ nuclear spin. Without the anisotropic part the Hamiltonian is

$$H_0 = \begin{pmatrix} \frac{a}{4} - \frac{g_e\mu_B B_0}{2} - \frac{g_n\mu_n B_0}{2} & 0 & 0 & 0 \\ 0 & -\frac{a}{4} - \frac{g_e\mu_B B_0}{2} + \frac{g_n\mu_n B_0}{2} & \frac{a}{2} & 0 \\ 0 & \frac{a}{2} & -\frac{a}{4} + \frac{g_e\mu_B B_0}{2} - \frac{g_n\mu_n B_0}{2} & 0 \\ 0 & 0 & 0 & \frac{a}{4} + \frac{g_e\mu_B B_0}{2} + \frac{g_n\mu_n B_0}{2} \end{pmatrix},$$

which gives the energy eigenvalues.

$$E_0 = \left( \begin{array}{c} \frac{a}{4} - \frac{g_e\mu_B B_0}{2} - \frac{g_n\mu_n B_0}{2} \\ -\frac{a}{4} + \frac{g_e\mu_B B_0}{2} + \frac{g_n\mu_n B_0}{2} \\ \frac{a}{4} - \frac{g_e\mu_B B_0}{2} + \frac{g_n\mu_n B_0}{2} \\ \frac{a}{4} + \frac{g_e\mu_B B_0}{2} - \frac{g_n\mu_n B_0}{2} \end{array} \right)$$

$$\approx \left( \begin{array}{c} \frac{a}{4} - \frac{g_e\mu_B B_0}{2} - \frac{g_n\mu_n B_0}{2} \\ -\frac{a}{4} + \frac{g_e\mu_B B_0}{2} + \frac{g_n\mu_n B_0}{2} \\ \frac{a}{4} - \frac{g_e\mu_B B_0}{2} + \frac{g_n\mu_n B_0}{2} \\ \frac{a}{4} + \frac{g_e\mu_B B_0}{2} - \frac{g_n\mu_n B_0}{2} \end{array} \right).$$

The flip-flip and flip-flop transitions gives the separations of the peak patterns in the ESR spectrum. E.g. difference between flip-flop and allowed transition frequency

$$\Delta f_k = (E(3) - E_0(2)) - (E_0(4) - E_0(2)) = g_n\mu_n B_0 - \frac{a_k}{2}.$$

The components of

$$T_k = \begin{pmatrix} T_{xx} & T_{xy} & T_{xz} \\ T_{yx} & T_{yy} & T_{yz} \\ T_{zx} & T_{zy} & T_{zz} \end{pmatrix}$$
FIG. 5. Coordinate axis of $T_k$ tensor in Si lattice.

TABLE I. Values of isotropic and anisotropic superhyperfine constants for Si:P used in the calculations in kHz units. The class labels to which of the four lattice classes the shell belongs and Nr. refers to the number of lattice sites in the shell. The values are evaluated from the data of refs. $^a$$^b$$^c$.

| Shell | Site | Group | Nr | $T_{xx}$ | $T_{yy}$ | $T_{zz}$ | $T_{xy}$ | $T_{xz}$ | $T_{yz}$ |
|-------|------|-------|----|---------|---------|---------|---------|---------|---------|
| A     | 004  | 1     | 6  | 2981    | -20.7   | 41.4    | 41.4    | 0       | 0       |
| B     | 440  | 2     | 12 | 2254    | 17      | 17      | -34     | 106.2   | -39.8   |
| C     | 337  | 3     | 4  | 1649    | 0       | 0       | 5       | -5      | -5      |
| D     | 337  | 2     | 12 | 1117    | -1.8    | -1.8    | 3.6     | 16.6    | 22.2    |
| E     | 111  | 3     | 4  | 270     | 0       | 0       | 700     | 700     | 700     |
| F     | 331  | 2     | 12 | 840     | -58.2   | -58.2   | 116.4   | -28.2   | -11.8   |
| G     | 777  | 2     | 12 | 764     | -2.5    | -2.5    | 5       | -1.2    | 5       |
| H     | 444  | 3     | 4  | 689     | 0       | 0       | 50.6    | -50.6   | 50.6    |
| I     | 228  | 2     | 12 | 685     | 8.7     | 8.7     | -17.4   | 27.8    | 13.8    |
| J     | 221  | 2     | 12 | 612     | 20.3    | 20.3    | -40.6   | 49.6    | 35.6    |
| M     | 221  | 2     | 12 | 612     | 8.7     | 8.7     | -17.4   | 27.8    | 13.8    |
| O     | 444  | 3     | 4  | 598     | 0       | 0       | 32.6    | 32.6    | 32.6    |
| Q     | 115  | 2     | 12 | 524     | 20.3    | 20.3    | -40.6   | 49.6    | 35.6    |
| R     | 771  | 2     | 12 | 379     | -10.5   | -10.5   | 21      | 0.2     | 19.4    |
| X     | 551  | 2     | 12 | 317     | -14.7   | -14.7   | 29.4    | 23.6    | 32.2    |

$a$ G. Feher, Phys. Rev., 114 (1959) 1219.
$b$ E. Hale and R. Mieher, Phys. Rev., 184 (1969) 739.
$c$ J. Ivey and R. Mieher, Phys. Rev. B, 11 (1975), 849.

are listed in Table I. Due to the symmetry of the silicon crystal the lattice sites can be divided into lattice shells ($A, B, C, \ldots$) for which the $T_k$ tensors are not independent. Every lattice site in the crystal belongs to one of the shells. In addition, each shell can be assigned to one of 4 classes ($S_1, S_2, S_3$ and $S_4$) depending on the symmetry of the shell. There are 6 independent components in $T_k$ in most general case which is the class $S_4$. For all the other classes only $\leq 4$ components are needed. All the closest lattice sites belongs to the first 3 classes ($S_1 - S_3$). The symmetry constraints of $T_k$ components for each shell are taken from ref. [21] and together with the requirement of $\text{Tr}[T] = 0$ all the components of $T_k$ can be calculated. These components are listed in Table I for some of the closest shells.

Now, if $T_k$ is known for any nuclei in a shell, the others can be evaluated by using rotations of the shell class,
exchanging any of the two nuclei in the shell and not influencing the lattice or the dopant structure \( [21] \). This can be achieved with a combination of two rotation operators \( R_x(\theta) \) and \( R_y(\theta) \) rotating the lattice around x- and y-axis shown in Table II. Finally the whole lattice is rotated so that the \( B_0 \) field is aligned with the 111-axis (angle \( \theta = 54.74^\circ \)). The transformed components \( T'_{ik} \) are then given by

\[
T'_{ik} = R_x^T[-\theta] \cdot R_y^T[-\pi/4] \cdot R_i[\theta] \cdot R_j[\theta] \cdot T_k \cdot R_y^T[\theta] \cdot R_x^T[-\pi/4] \cdot R_x[-\theta],
\]

where \( R_i \) and \( R_j \) are x and y rotations of angles \( \theta_i \) and \( \theta_j \) (Table II) depending on the class of the shell. Now, we make high field approximation \( |T_{ij}| << |g_e \mu_B B_0| \) and neglect the components of \( T_k \) connecting different electron spin states \( [13] \). The full Hamiltonian is then

\[
H = H_0 + \begin{pmatrix}
\frac{x'}{4} & \frac{t'}{4} & -\frac{t'j}{4} & 0 & 0 \\
\frac{t'}{4} & \frac{x'}{4} & -\frac{t'}{4} & 0 & 0 \\
\frac{t'}{4} & \frac{t'}{4} & \frac{x'}{4} & 0 & 0 \\
0 & 0 & -\frac{t'}{4} & \frac{t'}{4} & \frac{x'}{4} \\
0 & 0 & -\frac{t'}{4} & -\frac{t'}{4} & \frac{x'}{4}
\end{pmatrix}
\]

The ESR transition probabilities between the eigenvectors of eq. 5 \( \phi_i \) ja \( \phi_j \) are given by the Fermi’s golden rule

\[
P_{ij} = C \langle \phi_i | S_x | \phi_j \rangle,
\]

where \( C \) is a constant depending on the cavity and the excitation power, which was not accurately known in the experiments. In Table III we list the flip-flop transition probabilities divided by the the allowed ones

\[
\Gamma_k = \frac{\langle \uparrow \downarrow | S_x | \uparrow \downarrow \rangle_k}{\langle \uparrow \uparrow | S_x | \uparrow \downarrow \rangle_k}.
\]

The calculation gives equal values for the flip-flip and flip-flop transition probabilities.

For comparing the observed spectra to the calculated values we used a fitting function

\[
S(\Delta f) = A \sum_{k=1}^{90} (1 - \exp(-\Gamma_k t_p)) G_k(\Delta f),
\]

where \( G_k(\Delta f) = (C \sqrt{2\pi})^{-1} \exp(-\frac{1}{2}(\Delta f + f_k)^2) \), \( t_p \) is the effective ESR pumping time (depends on the excitation field strength) and \( C \) is the linewidth. The eq. 6 was fitted for the first 10 shells around \( P \) with significant \( \Gamma_k \) and with \( A, t_p \) and \( C \) as the fitting parameters.
TABLE III. Superhyperfine energies including anisotropic interaction and flip-flop transition probabilities $\Gamma_k$ for the six first shells in Si:P. Transition probabilities are given relative to the allowed transition probabilities.

| Shell | Nr. | Energy (kHz) | $\Gamma_k (10^{-9})$ |
|-------|-----|--------------|----------------------|
| A     | 3   | 2994.80      | 15.89                |
| A     | 3   | 2967.19      | 397.0                |
| B     | 3   | 2315.92      | 508.5                |
| B     | 3   | 2262.84      | 1431                 |
| B     | 3   | 2218.59      | 287.6                |
| C     | 1   | 1654.00      | 0                    |
| C     | 3   | 1647.33      | 3.677                |
| D     | 3   | 1137.33      | 4.440                |
| D     | 3   | 1111.47      | 72.01                |
| D     | 3   | 1107.73      | 40.94                |
| E     | 1   | 970.00       | 0                    |
| E     | 3   | 35.27        | 71800                |
| F     | 3   | 849.38       | 801.3                |
| F     | 3   | 838.43       | 1689                 |
| F     | 3   | 822.71       | 1338                 |