Dynamic Nuclear Polarization of Phosphorus in Silicon in Strong Magnetic Fields and Low Temperatures

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(Dated: March 13, 2014)

We report on electron spin resonance study of dynamic nuclear polarization (DNP) and relaxation of phosphorus donors in silicon in a magnetic field of 4.6 T and at temperatures below 1 K. The DNP occurs due to the Overhauser effect following a cross relaxation via the forbidden flip-flop or flip-flip transitions. Nuclear polarization values $P > 0.98$ were reached after 20 min of pumping with 0.4 $\mu$W of microwave power. An inverse sign DNP has been created by pumping the low field ESR line of P followed by the flip-flop cross relaxation. We observed a non-exponential behavior of the DNP and the subsequent relaxation, which may be explained by the polarization and spin diffusion of $^{29}$Si nuclei surrounding the $^{31}$P donors.

PACS numbers: 76.70.-r,76.30.-v,76.60.Es,71.55.Cn

Shallow donors in silicon P, As and Bi have been studied extensively since the pioneering experiments of Feher[1]. A revived interest to these systems has been raised by a recent proposal of using donor spins as qubits for quantum computing[2]. A long coherence time and ease of qubit initialization by external microwave fields are necessary conditions for building a quantum computer. These properties, also known as long transversal relaxation time and fast dynamic nuclear polarization, are inherent features of P impurities in Si (Si:P) at cryogenic temperatures. Despite of the numerous studies, Si:P system has not been thoroughly investigated in strong magnetic field[3] and at temperatures of $\approx 3$ K. The nuclear relaxation rate turned out to be fast in these conditions which, regardless of the high electron spin polarization ($> 98\%$), limited reaching a higher polarization. Typically in DNP experiments relatively high values of microwave power (up to 1 W) were used for irradiating Si:P samples.

In the present work we cooled Si:P samples to $\approx 0.2$ K, which led to a decrease of the nuclear relaxation rate to immeasurably small values and allowed reaching nuclear polarization $P > 0.98$ after excitation of 20 minutes. We evaluate that extremely pure nuclear spin states with $1 - P < 10^{-11}$ can be produced with sub-$\mu$W power levels. The nuclear spins are polarized by the Overhauser effect, involving relaxation via the forbidden transition with simultaneous electron and nuclear spin flips. We evaluated the cross relaxation rate by measuring the rate of the DNP, in which the flip-flop transition is the limiting step.

The experimental cell (SC) with the Si:P sample was placed in the center of a superconductive magnet producing a field of 4.6 T and cooled down by a dilution refrigerator. The sample of crystalline silicon with natural abundance, $2\times 2\times 0.07$ mm in size and doped by $6.5\times 10^{16}$ cm$^{-3}$ of P, was placed onto the flat mirror of a Fabry-Perot resonator (FPR) having a Q of approximately 4000. The crystal’s [111] axis was directed along the axis of the FPR resonator and polarizing magnetic field. ESR spectra from the sample were detected with a cryogenic heterodyne spectrometer[4] operating at 128 GHz. The spectrometer provides both absorption and dispersion signal components without a modulation of the magnetic field and is optimized for reaching high sensitivity at a small excitation power. This is important when studying samples with long electron spin-lattice relaxation times ($T_{1e} \approx 0.2$ s in our case). To avoid the saturation of Si:P ESR lines below 1 K we had to use a very low microwave power for detection, typically below 1 pW. For pumping the ESR lines in the DNP experiments we used the maximum available microwave power of 0.4 $\mu$W, which will be further referred to as pumping power.

The CW ESR absorption spectrum of a Si:P sample recorded just after cooling down to a low temperature is shown in the upper trace of Fig. 1. The spectrum consists of two lines corresponding to the allowed $a$-$d$ (low field) and $b$-$c$ (high field) transitions, separated by $\approx 42$ G due to the hyperfine interaction of $^{31}$P electron with its own nucleus. The lines are inhomogeneously broadened by the spin-$1/2$ $^{29}$Si nuclei of the host lattice.
which reside inside the relatively disperse electron cloud of $^{31}$P electron 1.

First, we performed a DNP experiment by saturating the allowed $b\rightarrow c$ transition. The magnetic field was set to the center of the $b\rightarrow c$ line and the excitation power was increased to the pumping value, aiming at full saturation of the ESR transition. For increasing the efficiency of the DNP the ESR excitation frequency was modulated with the frequency deviation corresponding to $3-4$ line widths and with the modulation rate of $10-20$ Hz. Since the electron spin-lattice relaxation time $\approx 0.2$ s is substantially longer than the modulation period, all the spin packets in the ESR line are simultaneously saturated. After pumping the $b\rightarrow c$ transition for a time $t_p$, the spectrometer was switched to detection power, and undistorted spectra with both ESR lines were recorded. Then, the nuclear polarization $P(t) = (n_a - n_b)/(n_a + n_b)$ was calculated from the ESR absorption line areas, which are proportional to the populations $n_a$ and $n_b$ of the $a$ and $b$ states. The polarization measurement was performed shortly ($< 50$ s) after the pumping, so that the nuclear state populations were not influenced by the nuclear relaxation, which turned out to be very slow below 1 K.

The spectra after $t_p = 30$ s and $t_p = 20$ min are shown in the 2nd and 3rd traces of Fig. 1. The DNP occurs due to the Overhauser effect, which transfers the population as: $b\rightarrow c\rightarrow a$ (the dashed arrow in Fig. 1 inset).

Due to the high $Q$ of the FPR and long spin-lattice relaxation time of the $^{31}$P electrons, the allowed $b\rightarrow c$ transition is fully saturated in a fraction of a second. It is clear that the DNP rate is limited by the much slower relaxation via the forbidden $a\rightarrow c$ transition, characterized by a cross-relaxation time $T_{ac}$. As we shall see below, the nuclear polarization can be negative if $n_a < n_b$. Therefore, to check whether the DNP behaves exponentially, we plotted $(1-P(t))$ in log units in Fig. 2. One can see that the polarization dynamics deviates strongly from an exponential at the beginning of the pumping. The characteristic time of the DNP build-up is $T_{ac} \approx 15$ s at the beginning and $T_{ac} \approx 1100$ s at the end, when the function is almost exponential. We estimate that the polarization $P > 0.98$ was reached in this experiment, based on the signal-to-noise ratio of $\approx 100$ since the $b\rightarrow c$ ESR line vanishes in the noise after $\approx 20$ min of pumping.

Next, we pumped the $a\rightarrow d$ transition. In this case the Overhauser effect leads to a DNP resulting in the population transfer $a\rightarrow d\rightarrow b$ and the creation of negative polarization where $n_a < n_b$. The result of this experiment is shown in the trace 4 of Fig. 1. The rate of the process is substantially slower than the other cross relaxation $b\rightarrow c\rightarrow a$. The polarization was increased by a factor of 2 after about 10 h pumping. Since the DNP in this case is limited by the flip-flip relaxation, we estimated the corresponding relaxation time $T_{bd}$ to be $\approx 5 \times 10^4$ s. This is $\geq 50$ times larger than $T_{ac}$.

We repeated the two pumping experiments at temperatures of 0.2 and 1 K and found out that the pumping dynamics follows a similar non-exponential behavior at approximately the same rate. This indicates that the relaxation rate via the forbidden transitions has a weak temperature dependence below 1 K. Another possible pathway for the DNP would be via the nuclear relaxation between the upper hyperfine states: $c \leftrightarrow d$. In this case, the slowest process, $c\rightarrow d$ nuclear relaxation, will mediate the transfer rate. However, as we shall see below, the nuclear relaxation rate has a very strong temperature dependence, which contradicts with the observation that $T_{ac}$ is temperature independent.

FIG. 1. (Color online) The ESR absorption spectra demonstrating DNP of P in silicon. Traces 1, 2 and 3 demonstrate the Overhauser effect: pumping the $b\rightarrow c$ transition, followed by the forbidden $c\rightarrow a$ relaxation. Trace 1 - before pumping, trace 2 - after 100 s pumping and trace 3 - after 20 min pumping. Trace 4 - demonstrates the result of pumping $a\rightarrow d$ transition with the relaxation via the $d\rightarrow b$ transition. The transfer of hyperfine level populations is shown in the level diagram on the right. Solid arrows denote the allowed ESR transitions and dashed traces relaxations via the forbidden flip-flop (upper diagram) and flip-flip (lower diagram) transitions.

FIG. 2. (Color online) Dynamics of the DNP process via the Overhauser effect when pumping the $b\rightarrow c$ transition. Log $1-P(t)$ is plotted as a function of pumping time $t_p$. The line is a guide for the eye.
At temperatures above 1 K, weak signals from the b-c line were observed even after pumping it for a very long time $t_p \gg T_{ac}$. Since the nuclear a-b relaxation is a mechanism competing with DNP, this process can be responsible for the decrease of the maximum DNP value observed at higher temperatures. To verify this, the nuclear a-b relaxation was studied as a function of temperature. We prepared starting conditions where all of the spins were in the a-state by pumping the b-c ESR line as described above. The temperature was kept at the lowest value of 0.2 K, where the nuclear polarization does not relax within several days. Then, the sample cell was rapidly warmed up and the temperature was stabilized to a desired value between 0.75 and 2.2 K. The evolution of the spin states towards the thermal equilibrium was monitored by measuring repeatedly the ESR spectrum with the detection power. An example of measurement results is shown in Fig. 3 with the curve starting with $P_0 \approx 0.6$ and $P_0 \approx 0.3$. The lines are bi-exponential fits to the data. The data for different starting polarization values at 1.37 K. The electron polarization was enhanced to $P_0 \approx 0.6$. The subsequent nuclear relaxation measurement revealed that the relaxation was much faster at the same $P$ value than it was when the measurement was started after the longer pumping with $P_0 \approx 1$. A similar result was found after repeating this measurement for an even smaller starting polarization ($P_0 \approx 0.3$). The slopes of the relaxation curves were quite the same at the beginning, meaning that the $T_{ab}'$ does not depend on the starting value of the nuclear polarization.

It is well known from the theory of the Overhauser effect [1], that in the high temperature limit ($g_e \mu_B B \ll k_B T$) the DNP enhancement over the thermal polarization is given by the ratio of the electron and nuclear gyromagnetic ratios $\gamma_e/\gamma_N$, which is $\approx 1600$ for $^{31}$P. However, this is not a correct result in high fields and low temperatures, when the electron polarization is very high and the nuclear spins are nearly unpolarized. At these conditions a much larger polarization enhancement can be reached. A microwave excitation saturating fully the electronic b-c transition for a long enough ($t_p \gg T_{ac}$) time will establish thermal equilibrium between $a$ and $c$-states and therefore $n_b = n_c \approx n_a \exp(-g_e \mu_B B/k_B T)$. After switching off the pumping, all the atoms in $c$-state will quickly relax to $b$-state, and we get the relation

$$n_a(n_b)_{DNP} = \frac{n_a}{2n_c} = \frac{1}{2} e^{-g_e \mu_B B/k_B T}.$$  \hspace{1cm} (1)

At 4.56 T and 0.2 K this gives a theoretical limit of the Overhauser DNP: $n_a/n_b \approx 10^{13}$.

So far we have neglected the nuclear relaxation, which will transfer atoms back from $a$ to $b$-state reducing the nuclear polarization. If the DNP enhancement is balanced by the nuclear relaxation and $n_a \gg n_b$, then from the kinetic equation for $a$-state

$$\frac{dn_a}{dt} = \frac{n_c}{T_{ac}} - \frac{n_a}{T_{ab}} = 0,$$  \hspace{1cm} (2)
follows that the maximum equilibrium value for the nuclear populations is

$$\left(\frac{n_a}{n_b}\right)_{max} = \frac{n_a}{2n_e} = \frac{T_{ab}}{2T_{ac}}. \quad (3)$$

The nuclear relaxation time in insulating solids is determined by the fluctuations of electron spins, and is proportional to electron polarization \[ \frac{\Delta}{k_B} \approx 6.2 \text{ K} \] with the pre-exponent of Eq. (1) being close to \( g_e \mu_B B/k_B \approx \frac{9(7)}{\text{K}} \). Within the temperature range of our current work, the forbidden relaxation time seems to be temperature independent. Therefore from Eqs. (3) and (4), with \( \Delta/k_B \approx 6.2 \text{ K} \), and long relaxation times in Fig. 4 coincides well with Eq. (4), with \( T_{ac} \), for the DNP of \( ^{31}\text{P} \) can be explained by difference in the polarization of the neighboring \( ^{29}\text{Si} \). The rate of spin diffusion is substantially slower inside the so-called spin diffusion barrier \[ ^{29}\text{Si} \] which is about 10 nm around \( P \) donors in our case, and is comparable to the mean distance between donors which is approximately 25 nm. We attribute the slow \( T_{ac} \) to the slow spin diffusion inside the spin diffusion barrier.

The temperature dependence of our data for the short and long relaxation times in Fig. 4 coincides well with Eq. (4), with \( \Delta/k_B = 5.9(7) \text{ K} \), when \( B/K_B \approx 6.2 \text{ K} \). Within the temperature range of our current work, the forbidden relaxation time seems to be temperature independent. Therefore from Eqs. (3) and (4), it follows that the maximum polarization, limited by the nuclear relaxation, has the same temperature dependence as that for the theoretical limit of Overhauser DNP (Eq. 1). From the pre-exponent of \( T_{ac} \) calculated from our data, we found that the maximum polarization is reduced by two orders of magnitude from the theoretical limit of Overhauser DNP (Eq. 1) due to the nuclear relaxation. Including this effect at \( T = 0.2 \text{ K} \), we get from Eq. (3) an estimate of \( \frac{n_a}{n_b} \approx 5 \times 10^{11} \). Reaching very high values of the DNP then actually becomes only a matter of time at these conditions. Pumping for a couple of hours (\( t_p \sim 5T_{ac} \)) will increase \( \frac{n_a}{n_b} \) by three orders of magnitude. The DNP can be done with very low values of the pumping power, enough for fully saturating the allowed ESR transitions, which is less than 1 \( \mu \text{W} \) in our case.

To our knowledge, the non-exponential DNP and relaxation have not been previously observed in the Si:P system, and are rather unusual in general. The two totally different time scales showing up in the DNP and relaxation indicate that the dynamics are complicated, probably involving multiple simultaneous spin flips. For the normal isotope composition, the \( ^{29}\text{Si} \) nuclear spins play an important role in the spin dynamics of shallow donors \[ ^{29}\text{Si} \]. Therefore, as a possible explanation of the bi-exponential behavior, we consider processes involving polarization of the \( ^{29}\text{Si} \) nuclei which are located in the neighboring lattice sites around the donors. The nuclear spin flips of the \( ^{29}\text{Si} \) have a back action on the electron spins \[ ^{29}\text{Si} \], and due to this we should consider a multi-spin system of a donor electron and nucleus coupled with several \( ^{29}\text{Si} \). The degree of polarization of \( ^{29}\text{Si} \) influences the rate of the \( a-b \) relaxation and the DNP in opposite ways.

The non-exponential dynamics can be explained if we consider a following process. At the beginning of a pumping the majority of the \( ^{29}\text{Si} \) near the donors are unpolarized. Polarization of these nuclei during \( T_{ac} \) also accelerates the cross-relaxation of the \( ^{31}\text{P} \). This explains the observed fast initial part of the DNP dynamics. Once all the \( ^{29}\text{Si} \) get polarized, the rate of DNP is reduced. Then, the process of spin diffusion leads to propagation of the \( ^{29}\text{Si} \) polarization to the regions far away from the donor atoms, thus creating a DNP of the bulk of the sample \[ ^{29}\text{Si} \]. Therefore, the two observed time scales, fast \( T_{ac} \) and slow \( T_{ac} \), for the DNP of \( ^{31}\text{P} \) can be explained by difference in the polarization of the neighboring \( ^{29}\text{Si} \). The rate of spin diffusion is substantially slower inside the so-called spin diffusion barrier \[ ^{29}\text{Si} \] which is about 10 nm around \( P \) donors in our case, and is comparable to the mean distance between donors which is approximately 25 nm. We attribute the slow \( T_{ac} \) to the slow spin diffusion inside the spin diffusion barrier.

In summary, from the evolution of the spin polarization during the DNP and the nuclear relaxation measurements, we conclude that the polarization of neighboring \( ^{29}\text{Si} \) spins has an important role in the dynamics of the \( ^{31}\text{P} \) nuclear spins. Unpolarized \( ^{29}\text{Si} \) spins increase the rate of the DNP whereas polarized spins increase the rate of the relaxation. We believe that the possibility of creating ensembles of nuclear spins in ultra-pure spin states demonstrated in this work may find useful applications, e.g. in the field of quantum computing.

We would like to thank K. Itoh, K. Kono, D. Konstantinov, and A. Tyryshkin for useful discussions. We acknowledge the funding from the Wihuri Foundation and the Finnish academy grants No. 260531 and 268745.

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