Long-lived spin echoes in magnetically diluted system: an NMR study of the Ge single crystals

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Quantum computing and NMR

Drastic developments in quantum computing using Nuclear Magnetic Resonance (NMR).

The main idea of quantum computer (QC) is to replace the classical bit by the quantum bit, or qubit, a quantum two-level system, which may be though as the spin-up and spin-down states of a spin $\frac{1}{2}$ particle.

Among different QC concepts, nuclear spins in semiconductor crystals, particularly in Si and Ge, are considered to be the ideal quantum bits.
Why nuclear spins?
Nuclear spins are naturally embodied in crystal lattice, and the interaction between the nuclear spins and environment is weak.

Why semiconductors?
Well-developed semiconductor technology makes construction of the semiconductor-based large-scale quantum computer to be quite realistic.

Why Si and Ge?
The choice of Si and Ge is determined by the fact that in both these crystals only one isotope (\(^{29}\text{Si}\) among three stable Si isotopes and \(^{73}\text{Ge}\) among five stable Ge isotopes) has nuclear spin and therefore isotopic engineering of Si and Ge permits to control the density of nuclear spins and vary the spin decoherence time \(T_2\), a crucial parameter in spintronics and quantum computing where nuclear spin is used as a qubit.
In order to implement quantum computation based upon spins in semiconductors, a detailed understanding of spin dynamics in the materials is required.

What relaxation parameters are important? While $T_1$ is the time at which energy of spin system is exchanged with the environment, spin-spin relaxation time $T_2$ is the time at which information is exchanged and which manifests as the loss of phase coherence. Thus $T_2$ scale is the important time scale for quantum computation.

To this end, a number of NMR studies have been carried out in order to investigate the nuclear spin decoherence in silicon.
$^{29}\text{Si}$ spin echo measurements of the Si powders with the natural abundance of $^{29}\text{Si}$ isotope have brought an unusual result, showing different character of decoherence process after applying Hahn echo sequence, on the one hand, and Carr-Purcell (CP) and Carr-Purcell-Meiboom-Gill (CPMG) pulse sequences, on the other hand. Hahn echo sequence yields single exponential decay with the time constant $T_2 = 5.6\text{ ms}$, while CPMG sequence resulted in a double-exponential decoherence process, with time constants 15 and 200 ms.

Since all atoms in the cubic Si structure are equivalent, the origin of the observed bi-exponential decay is unclear. Possible explanation: appearance of stimulated echo induced by the CPMG pulse train.

$^{29}\text{Si}$ echo decay after APCP pulse sequence. Broken line - Gaussian fit, solid line - bi-exponential fit.


$^{29}\text{Si}$ Hahn echo decay (circles/crosses) and CPMG echo trains for four samples ($a$–$d$) with different doping. [A. E. Dementyev, D. Li, K. MacLeean, S. E. Barrett, *Phys. Rev. B* **68**, 153302 (2003)].
Room temperature $^{73}$Ge NMR spectra of the Ge-7.76% (top) and Ge-1% (bottom) single crystals. External magnetic field $B_0$ is applied along the [111] direction. Dashed lines show bi-Lorentzian fit.

In Ge crystal with natural isotope abundance the contributions to the NMR line width coming from the dipole-dipole interaction, quadrupole interaction and magnetic field inhomogeneity are of the same order of magnitude. In the isotopically diluted Ge-1% crystal, the dipole-dipole coupling is reduced. In spite of this, NMR spectrum of this crystal shows broader wings in comparison with the Ge-7.76% crystal, which is evidently caused by the worse crystal perfection and larger contribution coming from the first order quadrupolar coupling.

$^{73}$Ge NMR spectra in Ge single crystals with $f = 1\%$ and 7.76%: symmetric resonances, the line width $\Delta \nu \sim 110$ Hz.

**Dipolar contribution** to the line width, estimated using Van Vleck formula for Gaussian lineshape: $\Delta \nu = 70$ and $62$ Hz for $B_0// [111]$ and $B_0// [110]$.

**Magnetic field inhomogeneity** $\sim 2$-3 ppm ($\sim 30$ Hz).

**Quadrupolar contribution** to the line width comes from the quadrupole interaction of $^{73}$Ge nuclei ($I = 9/2$) with small random electric field gradient, resulting from the crystal imperfections that cause small local deviations from cubic symmetry at nucleus site, as well as from the isotopic disorder among Ge atoms. Both these effects result in the first order quadrupolar broadening of the resonance line.
We report on the first NMR study of $^{73}\text{Ge}$ nuclear spin decoherence in germanium single crystals with different abundance of the $^{73}\text{Ge}$ isotope. Spin-spin relaxation (decoherence) time $T_2$.

Both Hahn and solid echo are formed. Hahn echo is formed by the interactions that are linear in the spin operators of the resonant nucleus and requires some inhomogeneity of the applied magnetic field. Decay of Hahn echo is caused by the interactions that are quadratic in the nuclear spin operators, such as dipolar and quadrupolar couplings, since the sign of these interactions is not changed by the $\pi$ pulse.

Solid (or “quadrupolar”) echo is formed by the interactions that are quadratic in the nuclear spin operators, i.e. by both dipolar and quadrupolar couplings, though the refocusing of these interactions by the solid echo sequence is not complete. Decay of the solid echo is caused by a modified (due to the second rf pulse) Hamiltonian of the above interactions, as well as by the inhomogeneity of the applied magnetic field.

All aforementioned contributions are present in the germanium, and both Hahn and solid echoes are formed in the crystals under study.
$^{73}\text{Ge}$ Hahn echo decay envelope in the linear and semi-logarithmic (insert) scales in Ge single crystal with natural abundance of $^{73}\text{Ge}$ isotope. External magnetic field is applied along the $[111]$ axis. Dashed and solid lines show single and bi-exponential fits, respectively.

$^{73}\text{Ge}$ NMR Hahn echo measurements

$$\left(\frac{\pi}{2}\right)_0 - \tau - (\pi)_{90} - \tau'-\text{echo}$$

7.76% of $^{73}\text{Ge}$

Accurate measurement of the Hahn echo decay envelopes in germanium crystal with natural abundance of $^{73}\text{Ge}$ isotope yields non-exponential echo decay.
$^{73}\text{Ge}$ NMR solid echo measurements

$$
\left(\frac{\pi}{2}\right)_0 - \tau - \left(\frac{\pi}{2}\right)_{90} - \tau' - \text{echo}
$$

7.76% of $^{73}\text{Ge}$

$^{73}\text{Ge}$ solid echo decay envelope in the linear and semi-logarithmic (insert) scales in Ge single crystal with natural abundance of $^{73}\text{Ge}$ isotope. External magnetic field is applied along the [110] axis. Dashed and solid lines show single and bi-exponential fits, respectively.

Hahn and solid echo decays may be well fit by a superposition of two exponentials:

$$
M(t) = M_1(0)\exp\left(-2\tau / T_{21}\right) + M_2(0)\exp\left(-2\tau / T_{22}\right)
$$
73Ge NMR Hahn and solid echo measurements

1 % of 73Ge

$B_0 // [111]$ 

Deviation from the single exponential is much more pronounced in measurements of the germanium crystal with 1% of 73Ge. In this crystal, both Hahn and solid echo decay envelopes exhibit strikingly non-exponential behavior, producing long-lived echoes.

73Ge Hahn echo and solid echo decay envelopes in Ge single crystal with 1% of 73Ge isotope. External magnetic field is applied along the [111] axis. Thin solid lines show bi-exponential fits.
$^{73}$Ge NMR Hahn and solid echo measurements
1% of $^{73}$Ge
$B_0 // [110]$

$^{73}$Ge Hahn echo and solid echo decay envelopes in Ge single crystal with 1% of $^{73}$Ge isotope. External magnetic field is applied along the [110] axis. Thin solid lines show bi-exponential fits.
Experimental nuclear spin decoherence times $T_{21}$ and $T_{22}$ in Ge single crystals. Accuracy is around 10-15%.

<table>
<thead>
<tr>
<th></th>
<th>$T_{21}$, ms Hahn echo</th>
<th>$T_{22}$, ms Hahn echo</th>
<th>$T_{21}$, ms solid echo</th>
<th>$T_{22}$, ms solid echo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge-7.76% B // [111]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge-7.76% B // [110]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge-1% B // [111]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge-1% B // [110]</td>
<td></td>
<td></td>
<td></td>
<td>201</td>
</tr>
</tbody>
</table>

The decay of the echoes at the long-time domain, described by the time $T_{22}$, is slower with the reduced $^{73}$Ge abundance, and the ratio $T_{22}$(Ge-1%)/$T_{22}$(Ge-7.76%) is more or less close to the reciprocal ratio of the isotope contents. Statistical theory of NMR lineshape in magnetically diluted systems with dipolar coupling among the spins predicts an exponential FID and Lorentzian line shape with the line width proportional to the nuclear spin concentration ($\Delta \nu \sim f$). In such a case, $T_2$ should be inversely proportional to the isotope content. Therefore we are led to conclusion that the slow part of the decay is caused by the dipole-dipole interaction among nuclear spins and reflects the primary decoherence process in the spin system.
Origin of the fast echo decay at the beginning of the relaxation process.
Decay time $T_{21}$ is shorter in Ge-1% crystal than in Ge-7.76% crystal, and thus is not caused by the dipole-dipole interaction. At that, the reduction in $T_{21}$ in the crystal with 1% of $^{73}$Ge correlates with the broader line wings observed in this crystal, which are caused by the quadrupole interaction. Conclusion: initial part of the echo decay is caused by the quadrupole interaction.

Qualitatively, the spectrum of Ge-1% crystal may be described as a sum of two lines: (i) central transition is not shifted by the first order quadrupole interaction, is broadened by dipole-dipole interactions only and therefore shows a narrow line, and (ii) the other transitions shifted in the first order by the quadrupole interaction and yield unresolved satellite lines (broad envelope).

In the time domain, these two components would cause two different decays, i.e. fast decay caused by the quadrupole interaction and slow decay caused by dipole-dipole interaction. Assuming the lineshapes to be Lorentzian, we would obtain a bi-exponential decay observed in the experiment with time constants $T_{21}$ and $T_{22}$ related to quadrupole and dipole couplings, respectively.
Theory

Calculations of the Hahn and solid echo decays. The amplitude of echo following a pulse sequence is described by the equation

\[
E(\tau', \tau) = \frac{1}{\text{Tr}(I^2_X)} \text{Tr} e^{iH\tau'} R \cdot e^{-iH\tau} I_X e^{iH\tau} R^{-1} e^{iH\tau'} I_X
\]

\(hH\) - secular terms of the spin Hamiltonian in the rotating frame, and operator \(R\) describes the action of the second rf pulse. \(R=\exp(-i\pi I_x)\) for Hahn echo.

The interaction Hamiltonian of the nuclear spin can be written as

\[
H = \sum_j H_j + \sum_{i<j} H_{ij}
\]

- sum of the interaction of nuclear spin with inhomogeneous magnetic field and quadrupolar coupling

\[
H_j = -\delta_j I_{Zj} + \omega_{Qj} \left( I^2_{Zj} - \frac{1}{3} I(I + 1) \right)
\]

- quadrupole frequency

\[
\omega_{Qj} = \frac{3e^2 QV^{(j)}_{zz}}{4I(2I - 1)}
\]

\[
H_{ij} = b_{ij} \left[ I_{Zi} I_{Zj} - \frac{1}{4} (I_i^+ I_{-j}^+ + I_{-i}^- I_{+j}^-) \right]
\]

- secular part of the dipole-dipole interaction

where

\[
b_{ij} = \frac{\eta \gamma^2 (1 - 3\cos^2 \theta_{ij})}{r_{ij}^3}
\]
Since the contributions to the echo response from different terms of the Hamiltonian can not be separated. This makes the calculation of the echo decays in analytic form to be impossible. Therefore, we use a simplified model neglecting the commutator; such approximation is equivalent to neglecting the flip-flop terms in the dipolar Hamiltonian and using it in the form

\[ H_{ij} = b_{ij} I_z I_z \]

Since the spin echo signal arises only in the case of spin ensemble with a spread of the resonance parameters, we introduced Lorentzian distribution of these parameters that is generally accepted for magnetically diluted systems in solids:

\[
f_d(d_j) = \frac{\Delta_d}{\pi} \frac{1}{d_j^2 + \Delta_d^2}
\]
\[
f_Q(\omega_Q) = \frac{\Delta_Q}{\pi} \frac{1}{\omega_Q^2 + \Delta_Q^2}
\]
\[
f(\delta_j) = \frac{\Delta}{\pi} \frac{1}{\delta_j^2 + \Delta^2}
\]

Here

\[ d_j = \sum_i b_{ij} I_z i \]

and \(\Delta\) is the half width at the half height.
Calculations result in an approximate expression for the echo amplitude

\[ E(2\tau) \approx 0.85 \exp\left(-2\tau / T_{21}\right) + 0.15 \exp\left(-2\tau / T_{22}\right) \]

where

\[ T_{21} = \frac{1}{5\Delta_Q} \]
\[ T_{22} = \frac{1}{\Delta_d} \]

and

for the Hahn echo

\[ T_{21} = \frac{1}{3.25\Delta_Q + \Delta_d + \Delta} \]
\[ T_{22} = \frac{1}{0.3(\Delta_d + \Delta)} \]

and

for the solid echo.

Realistic physical picture of spin-spin relaxation: Hahn and solid echo decays may be described by a superposition of two exponentials, in agreement with the bi-exponential \(^{73}\text{Ge}\) decays observed in the experiment.

Theory shows that rapidly relaxing component of the Hahn echo is caused by the quadrupole interaction, while the decay of the slowly relaxing component is caused by the dipole-dipole coupling, as expected according to the physical fundamentals.

For solid echo, the fast decay is caused by a combination of the quadrupole, dipole-dipole interaction and magnetic field inhomogeneity, while the slowly decaying part is caused by the dipole-dipole coupling and magnetic field inhomogeneity, which also follows from the physical fundamentals.
$\Delta_d$, $\Delta$, and $\Delta_Q$ (Hz) calculated from the experimental data using formulas for $T_{21}$ and $T_{22}$

<table>
<thead>
<tr>
<th>Isotope content</th>
<th>Method</th>
<th>$\Delta_Q$</th>
<th>$\Delta_d$</th>
<th>$\Delta_d +\Delta$</th>
<th>$\Delta_Q$</th>
<th>$\Delta_d$</th>
<th>$\Delta_d +\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge−7.76%</td>
<td>Hahn echo</td>
<td>34</td>
<td>63</td>
<td>-</td>
<td>28</td>
<td>59</td>
<td>-</td>
</tr>
<tr>
<td>Ge−7.76%</td>
<td>Solid echo</td>
<td>37</td>
<td>83</td>
<td>14</td>
<td>93</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge−1%</td>
<td>Hahn echo</td>
<td>111</td>
<td>5.4</td>
<td>-</td>
<td>114</td>
<td>7.8</td>
<td>-</td>
</tr>
<tr>
<td>Ge−1%</td>
<td>Solid echo</td>
<td>148</td>
<td>17.6</td>
<td>156</td>
<td>16.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Calculated dipolar line width in the Ge-7.76% crystal is of the same order of magnitude that expected from the Van Vleck's formula.

Calculated quadrupolar parameter $\Delta_Q$ is close to that estimated as half-width of the broader Lorentzian.

Evaluated magnetic field inhomogeneity is comparable with that produced by our magnet, though in the case of the Ge-1% crystal formula of $T_{22}$ yields understated estimate of $\Delta$.

Nevertheless, theory gives quite satisfactory description of the echo decays, in spite of approximate character of computations.
Eventual application of Ge as a material for quantum computer, in which $^{73}\text{Ge}$ nuclear spins are used as qubits.

One of the main goals in quantum computing is elongation of decoherence time $T_2$. To do this, one should prepare spin-diluted crystals in order to reduce dipole-dipole interactions. Nowadays, well-developed semiconductor technology allows successful isotopic engineering and growing the pure monoisotopic $^{70}\text{Ge}$ crystal enriched up to the level of 99.99%, which means that the content of $^{73}\text{Ge}$ isotope is less than 0.01%. Our findings, presented above, show that in such a crystal the decoherence time $T_2$ would be elongated up to ~20 s, which is quite an encouraging result for application of this material in Ge and SiGe structures, which are suggested in different proposals for experimental realization of nuclear spin-based quantum computers.
Summary

Our $^{73}\text{Ge}$ NMR measurements of Hahn and solid echo decay envelopes in germanium single crystals with different abundance of the $^{73}\text{Ge}$ isotope show that the echo decay is caused by two different decoherence processes.

The fast decay at the beginning of the relaxation process is mainly caused by the quadrupole interaction. Then this process proceeds to slowly decaying, long-lived spin echoes that are caused by dipole-dipole coupling among nuclear spins. This slow decay may be elongated by means of spin dilution.

Our experimental findings are supported by the calculations of Hahn and solid echo decays in the germanium crystals, which yield realistic physical picture of spin-spin relaxation.

Elongation of the slow component of the dephasing process with depletion of Ge crystal with $^{73}\text{Ge}$ isotope is encouraging for application of this material in Ge and SiGe structures for a nuclear spin-based quantum computer.
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A. N. Ionov, V. I. Ozhogin, A.V. Tikhomirov, Russian Research Center “Kurchatov Institute”, Moscow, Russia
"In the Negev will the talents of Jewish science and research be tested..." David Ben-Gurion

Thank you!
Individual control of the temporal evolution of the spins can be achieved with the use of external electromagnetic radiation, i.e. NMR or ESR pulses. The spins are coupled with each other via dipolar coupling or interaction mediated by the two-dimensional electron gas in the heterostructure. The internal interactions can be controlled by gates formed on top of the heterostructure. The spin-spin coupling causes decoherence of the qubits.

Electric field, applied to the gate A, pulls out the electron wave function from donor to barrier, reducing hyperfine coupling and thus the resonance frequency of nuclei.