Approximation of the Relaxation Time of Nuclei in Silicon at Room Temperature

Näherung der Relaxationszeit von Kernspins in Silizium bei Raumtemperatur

presented by

Tobias Herrig

Matrikelnummer: 336108

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Gutachter: Prof. Dr. David DiVincenzo

Zweitgutachter: Prof. Dr. Fabian Hassler

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1 Introduction

The paper *Room-Temperature Quantum Bit Storage Exceeding 39 Minutes Using Ionized Donors in Silicon-28* of Saeedi et al. (2013) [2] is about an experiment to measure the relaxation times T_1 and T_2 of nuclear spins in doped silicon. In this bachelor thesis I try to derive an approximate value for a contribution to the relaxation time of phosphor atoms in silicon at room temperature under the conditions of the experiment. The considered mechanism is the coupling of the nuclei to the spins of the free electrons and holes. The aim is to see if this mechanism can explain the experimental results on its own.

First, I will briefly introduce the Bloch equations and the relaxation times as theoretical framework. The conditions and the results of the experiment are described in the next section. After that I will start the calculation of the relaxation time T_1 analogously to deriving the Korringa relation, recapitulating the calculations made in the book of Slichter (1990) [4]. This will end up with an integral which has to be evaluated under the given conditions of the experiment. For that the quasi Fermi level for both the electrons and holes need to be calculated, which will be done in the next section. This section also deals with finding an appropriate way to handle the Fermi-Dirac distribution. And in the last section I will use the obtained results for solving the integral to get a final result for the contribution to the relaxation time.

2 Bloch Equations

Imagine a nucleus with a spin of 1/2 in an external constant magnetic field along the z-axis $\boldsymbol{B} = B \cdot \boldsymbol{e_z}$. In that case, the magnetic moment $\boldsymbol{\mu}$ precesses about the z-axis with the Larmor frequency $\omega_L = \gamma B$. Because of the Zeemann effect the energy levels are splitting up with $\Delta E = E_\downarrow - E_\uparrow = \hbar \cdot \omega_L = \hbar \cdot \gamma B$ with the gyromagnetic ratio γ. In a macroscopic material the summation over the single magnetic moments yields the magnetization

$$\boldsymbol{M} = \sum_i \boldsymbol{\mu_i}.$$

Then the Bloch equations can be formulated phenomenologically:

$$\frac{dM_x}{dt} = \gamma(\boldsymbol{M} \times \boldsymbol{B})_x - \frac{M_x}{T_2}$$
$$\frac{dM_y}{dt} = \gamma(\boldsymbol{M} \times \boldsymbol{B})_y - \frac{M_y}{T_2}$$
$$\frac{dM_z}{dt} = \gamma(\boldsymbol{M} \times \boldsymbol{B})_z + \frac{M_0 - M_z}{T_1}$$

Here, $M_0 = \chi_0 B$ is the equilibrium magnetization with the susceptibility χ_0. The first term in the Bloch equations describes the precession of the magnetization about the external field with the Larmor frequency ω_L and the second describes the relaxation with the characteristical times T_1 and T_2. So in equilibrium we obtain $\boldsymbol{M} = M_0 \cdot \boldsymbol{e_z}$. T_1 is called longitudinal relaxation time and is caused by several interactions, especially between the nuclei and the electrons and holes. T_2 is called transversal relaxation time (or spin-spin relaxation time) and is caused by interactions between the nuclear spins among each other, which leads to spin decoherence. Because of that, T_2 is also called coherence time. For the relaxation times it applies $T_2 \leq 2 \cdot T_1$ and in most situations T_1 is even bigger than T_2. If you solve the Bloch equations, you obtain with the initial magnetization $\boldsymbol{M}(0)$:

$$M_{x,y}(t) = M_{x,y}(0) \cdot e^{-\frac{t}{T_2}}$$
$$(M_z(t) - M_0) = (M_z(0) - M_0) \cdot e^{-\frac{t}{T_1}}$$

So, the Relaxation times are just the mean lifetimes of the magnetization components (more precisely, the components of the difference between the actual magnetization and the equilibrium magnetization).

3 Experiment

This section deals with the conditions of the experiment that are relevant for our theoretical treatment and its results. They can be looked up detailed in the paper of Saeedi et al. (2013) [2].

3.1 Conditions

In the experiment they used silicon enriched to 99.995% ^{28}Si containing $\sim 5 \cdot 10^{11} \, \text{cm}^{-3}$ of the donor phosphorus-31 and $\sim 5 \cdot 10^{13} \, \text{cm}^{-3}$ of the acceptor boron. Hence, it is a p-type semiconductor. The experiment involves three steps:

1. For the preparation of the sample, a 1047 nm laser photoneutralizes all the donors and acceptors. They optically hyperpolarize[1] the spins of the neutral donor states (D^0) and then fully ionize the donors for the measurements, because the electrons of the neutral D^0 states were causing decoherence and therewith a decrease of T_2.

2. While the relaxation processes, the sample gets manipulated to avoid noise and interference caused by fluctuations.

3. The last step is the readout of the remaining spin population.

They used two different temperature profiles; either a fixed temperature at $T \leq 4.2 \, \text{K}$ or a temperature at $4.2 \, \text{K}$ during the preparation and the readout while the temperature during the relaxation process and the manipulation is hold at room temperature (298 K).

3.2 Results

For the T_1-relaxation they got a result of 78 min at 298 K and $T_1 \gg 1 \, \text{h}$ at 1.9 K. For the coherence time at cryogenic temperatures they reached $T_2 = 180 \, \text{min}$ at 1.2 K and with room temperature they obtained $T_2 = 39 \, \text{min}$.

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[1]Hyperpolarization is a state in which the degree of alignment of nuclear spins is far beyond thermal equilibrium.

4 Calculations on T_1 from Slichter

As already mentioned, we consider the T_1-relaxation of the nuclei by their coupling to the spins of the free electrons and holes. This leads to a derivation similar to deriving the Korringa relation (cf. Slichter, 1990 (pp.151-157) [4]), which considers the degenerate case[2] for metals.

In this mechanism, a nuclear transition is coupled with a simultaneous electron (or hole) transition in order to conserve energy. The number of transitions per unit time between the initial state of nucleus and electron (or hole) $|m\boldsymbol{k}s\rangle$ and the final state $|n\boldsymbol{k}'s'\rangle$ is determined by Fermi's Golden Rule (m, n are the nuclear quantum numbers and $\boldsymbol{k}$, s, $\boldsymbol{k}'$, s' are the wave vectors and spin orientations of the electron or hole.):

$$W_{m\boldsymbol{k}s,n\boldsymbol{k}'s'} = \frac{2\pi}{\hbar} \left| \langle m\boldsymbol{k}s|V|n\boldsymbol{k}'s'\rangle \right|^2 \delta(E_m + E_{\boldsymbol{k}s} - E_n - E_{\boldsymbol{k}'s'}) \qquad (4.1)$$

The initial electron (or hole) state has to be occupied while the final state has to be unoccupied. Therefore, we have for the total nuclear transition probability

$$W_{mn} = \sum_{\boldsymbol{k},s,\boldsymbol{k}',s'} W_{m\boldsymbol{k}s,n\boldsymbol{k}'s'} f(\boldsymbol{k},s)[1 - f(\boldsymbol{k}',s')]. \qquad (4.2)$$

The interaction from the s-state coupling between the nuclear and the electron spins is[3]

$$V = \frac{2}{3}\mu_0 \gamma_e \gamma_n \hbar^2 \boldsymbol{I} \cdot \boldsymbol{S} \delta(\boldsymbol{r}) \qquad (4.3)$$

γ_n is the gyromagnetic ratio of the nucleus, so in this case, of phosphorus. With Bloch's theorem we get $|m\boldsymbol{k}s\rangle = |m\rangle |s\rangle u_{\boldsymbol{k}}(\boldsymbol{r}) \exp(i\boldsymbol{k} \cdot \boldsymbol{r})$. And using

$$\sum_{s,s'} \langle s|S_\alpha|s'\rangle \langle s'|S_{\alpha'}|s\rangle = \frac{\delta_{\alpha\alpha'}}{2},$$

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[2]In the degenerate case, the Fermi level lays inside one of the energy bands.
[3]Different as in the book of Slichter, we use SI units instead of Gaussian units

one obtains

$$W_{mn} = \frac{4}{9}\pi\hbar^3\mu_0^2\gamma_e^2\gamma_n^2 \sum_\alpha \langle m|I_\alpha|n\rangle \langle n|I_\alpha|m\rangle \cdot G(T),$$

$$=: a_{00} \sum_\alpha |\langle m|I_\alpha|n\rangle|^2$$

with

$$G(T) = \sum_{\boldsymbol{k},\boldsymbol{k'}} |u_{\boldsymbol{k}}(0)|^2 \, |u_{\boldsymbol{k'}}(0)|^2 f(E_{\boldsymbol{k},s})[1 - f(E_{\boldsymbol{k'},s'})]\delta(E_m + E_{\boldsymbol{k}s} - E_n - E_{\boldsymbol{k'}s'}).$$

Now, we can replace the summation over $\boldsymbol{k}$ and $\boldsymbol{k'}$ by an integral over $E_{\boldsymbol{k}}$ and $E_{\boldsymbol{k'}}$, introducing the density of states $\rho(E_{\boldsymbol{k}})$ and replacing the $|u_{\boldsymbol{k}}(0)|^2$ with the average over the energy surface $\langle|u_{\boldsymbol{k}}(0)|^2\rangle_{E_{\boldsymbol{k}}}$. And with a little approximation and integrating over the delta function, we obtain

$$G(T) = \int dE \, \langle|u_{\boldsymbol{k}}(0)|^2\rangle_E^2 \, \rho^2(E) \, f(E)[1 - f(E)]. \tag{4.4}$$

To finally get a equation involving the relaxation time T_1, Slichter [4] uses the following relation

$$\frac{1}{T_1} = \frac{1}{2}\frac{\sum\limits_{m,n} W_{mn}(E_m - E_n)^2}{\sum\limits_m E_m^2}$$

$$= -\frac{a_{00}}{2}\frac{\sum\limits_{m,n,\alpha} \langle m|[\mathcal{H}, I_\alpha]|n\rangle \langle n|[\mathcal{H}, I_\alpha]|m\rangle}{\sum\limits_m \langle m|\mathcal{H}^2|m\rangle}$$

$$= -\frac{a_{00}}{2}\frac{\sum\limits_\alpha Tr\{[I_z, I_\alpha]^2\}}{Tr\{I_z^2\}} \quad\Bigg|\; Tr\{I_\alpha^2\} = Tr\{I_{\alpha'}^2\}$$

$$= a_{00} = \frac{4}{9}\pi\hbar^3\mu_0^2\gamma_e^2\gamma_n^2 \cdot G(T) \tag{4.5}$$

So, we have reduced the problem to solving the integral (4.4).

In a semiconductor, the density of states near the band edge is for the conduction band (cf. Kittel and Kroemer, 1980 [5])

$$\rho_C(E) = \frac{V}{2\pi^2} \left(\frac{2m_e^*}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{E - E_C} \tag{4.6}$$

and for the valence band, respectively,

$$\rho_V(E) = \frac{V}{2\pi^2} \left(\frac{2m_h^*}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{E_V - E}, \tag{4.7}$$

with the effective masses of the electrons and holes m_e^* and m_h^*. E_C and E_V are the energies at the band edges of the conduction and the valence band, so that the band gap is $\Delta E_g = E_C - E_V$.

The distribution function for electrons and holes is the Fermi-Dirac distribution

$$f_{e/h}(E, E_F) = \frac{1}{1 + \exp\left(\pm \frac{E - E_F}{kT} \right)}, \tag{4.8}$$

where the $+$ is for electrons and the $-$ for holes. E_F is the Fermi level, which in generally is temperature-dependent and has to be calculated. Nevertheless, this integral over the Fermi distribution is not precisely analytically solvable, therefore we have to make an appropriate approximation. The most often used approximation is the Boltzmann distribution, which applies if $\exp\left(\pm \frac{E - E_F}{kT} \right) \gg 1$:

$$f_{e/h}(E, E_F) = \frac{1}{1 + \exp\left(\pm \frac{E - E_F}{kT} \right)} \approx \exp\left(\mp \frac{E - E_F}{kT} \right). \tag{4.9}$$

When integrating over the conduction (valence) band, this means $E_C - E_F \gg kT$ ($E_F - E_V \gg kT$), so the Fermi level has to be somewhere in the band gap. This is called the non-degenerate case or the classical regime. So it is in more than one way interesting to know where the Fermi level lays (as a function of temperature).

5 Quasi Fermi Levels

Let n_e be the concentration of electrons in the conduction band and n_h the concentration of holes in the valence band. Let further $n_D^{(+)}$ be the concentration of (ionized) donors and $n_A^{(-)}$ the concentration of (ionized) acceptors. In a pure (or intrinsic) semiconductor the number of conduction electrons will be equal to the number of holes for all temperatures, if the crystal is electrically neutral. This means

$$n_e - n_h = 0. \tag{5.1}$$

This equation is called the neutrality condition. In the case of a doped semiconductor, we define $\Delta n \equiv n_D^+ - n_A^-$. Then the neutrality condition turns into

$$n_e - n_h = \Delta n = n_D^+ - n_A^-. \tag{5.2}$$

However, this relation implies a total thermal equilibrium between the electrons and holes, which does not apply in our situation (at least at not too high temperatures).[4]

At the end of the preparation of the sample, the donors gets optically ionized and their electrons are excited into the conduction band, while the holes in the valence band are in a thermal equilibrium with the holes in the acceptor states. Thus we have no longer one Fermi level E_F but two quasi Fermi levels, one for the conduction electrons E_F^{QC} and one for the holes in the valence band and the acceptor states E_F^{QV}.[5] So, we have to look at the electrons and holes separately.

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[4]To be exact, the neutrality condition even holds true in a quasi equilibrium, as in our case. But it is not helpful for calculating the quasi Fermi level (see below).

[5]More precisely, there is a third quasi Fermi level for the donor states, somewhere below their energy level E_D. But the ionization of the donor states do not change with temperature, so this is no interesting consideration.

5.1 Electrons

For the conduction electrons, neglecting the thermal excitation from the valence band, one has

$$n_D = n_D^+ = n_e = \frac{1}{V} \int\limits_{\text{conduction band}} dE \, \rho_C(E) f_e(E, E_F^{QC}), \qquad (5.3)$$

with V the volume of the crystal.

At cryogenic temperatures, we expect that the degenerate case applies and the quasi Fermi level lays in the conduction band, because of the non-vanishing number of conduction electrons at $0\,\text{K}$. With increasing temperature the quasi Fermi level should fall into the band gap and the classical regime should apply.

Since there will be only free carriers near the band edge, the higher limit of the integral can be chosen as ∞^6, giving us (using eq. (4.6) and (4.8))

$$\begin{aligned}
n_D &= \int\limits_{E_C}^{\infty} dE \, \frac{1}{2\pi^2} \left(\frac{2m_e^*}{\hbar^2}\right)^{\frac{3}{2}} \frac{\sqrt{E - E_C}}{1 + \exp\left(\frac{E - E_F^{QC}}{kT}\right)} \\
&= 2 \left(\frac{m_e^* kT}{2\pi\hbar^2}\right)^{\frac{3}{2}} \left(\frac{2}{\sqrt{\pi}} \int\limits_0^{\infty} dX \, \frac{\sqrt{X}}{1 + \exp\left(X - \eta\right)}\right) \\
&=: 2 \left(\frac{m_e^* kT}{2\pi\hbar^2}\right)^{\frac{3}{2}} \mathcal{F}_{1/2}(\eta),
\end{aligned}$$

where the substitution $X = (E - E_C)/kT$, $\eta = (E_F^{QC} - E_C)/kT$ has been made. $\mathcal{F}_j(\eta)$ is called the (complete) Fermi-Dirac integral. For $j = 1/2$ there is an approximation which is separately defined on two value domains and which relative error is not bigger than 3% (cf. Blakemore, 1982 [1]):

$$\mathcal{F}_{1/2} = \begin{cases} \dfrac{4}{3\sqrt{\pi}} \left(\eta^2 + \dfrac{\pi^2}{6}\right)^{\frac{3}{4}} & \text{for } 1.3 \leq \eta < \infty \\[3mm] \dfrac{1}{0.27 + \exp(-\eta)} & \text{for } -\infty < \eta < 1.3 \end{cases} \qquad (5.4)$$

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[6] The same trick will be used for the integration over the valence band, to set the lower limit to $-\infty$.

Using the approximation for $\eta < 1.3$, gives us

$$n_D = 2 \left(\frac{m_e^* kT}{2\pi\hbar^2} \right)^{\frac{3}{2}} \frac{1}{0.27 + \exp(-\eta)}$$

$$\Leftrightarrow \quad \eta(T) = -\ln \left\{ \frac{2}{n_D} \left(\frac{m_e^* kT}{2\pi\hbar^2} \right)^{\frac{3}{2}} - 0.27 \right\} \tag{5.5}$$

$$\Leftrightarrow E_F^{QC}(T) = E_C - kT \ln \left\{ \frac{2}{n_D} \left(\frac{m_e^* kT}{2\pi\hbar^2} \right)^{\frac{3}{2}} - 0.27 \right\}. \tag{5.6}$$

To check the applicability of the approximation, one can calculate the value $\eta(T = 0.1K) = -5.8 < 1.3$ which shows that the degenerate case applies only for very low temperatures, due to a low donor concentration. One can further calculate $\eta(T = 0.1K)$ for the classical regime. One obtains the equation for the classical regime by dropping the 0.27 in equations (5.4)-(5.6), which gives us the same value up to the third decimal place. So, the Boltzmann distribution is even at cryogenic temperatures a good approximation for the Fermi distribution. This gives us

$$n_e = \frac{1}{V} \int_{E_C}^{\infty} dE \, \rho_C(E) f_e(E, E_F^{QC})$$

$$= 2 \left(\frac{m_e^* kT}{2\pi\hbar^2} \right)^{\frac{3}{2}} \exp \left(\frac{E_F^{QC} - E_C}{kT} \right) \underbrace{\left(\frac{2}{\sqrt{\pi}} \int_0^{\infty} dX \, \sqrt{X} \exp(X) \right)}_{=1} \tag{5.7}$$

and analogously

$$n_h = \frac{1}{V} \int_{-\infty}^{E_V} dE \, \rho_V(E) f_h(E, E_F^{QV}) = 2 \left(\frac{m_h^* kT}{2\pi\hbar^2} \right)^{\frac{3}{2}} \exp \left(-\frac{E_F^{QV} - E_V}{kT} \right). \tag{5.8}$$

Going now to higher temperatures, the thermal excitation between the valence and the conduction band will not be neglectible anymore. From this point onwards, a thermal equilibrium between the electrons and holes could arise. The thermally generated conduction electrons can (in good approximation) be described with the Fermi distribution for an intrinsic semiconductor.

Thus, to take account for those extra conduction electrons, one can add an extra term to eq. (5.3):

$$n_D = n_e - \frac{1}{V} \int\limits_{E_C}^{\infty} dE \, \rho_C(E) f_e(E, E_F^0)$$

$$\Leftrightarrow n_D = 2 \left(\frac{m_e^* kT}{2\pi\hbar^2} \right)^{\frac{3}{2}} \left[\exp\left(\frac{E_F^{QC} - E_C}{kT} \right) - \exp\left(\frac{E_F^0 - E_C}{kT} \right) \right]$$

$$\Leftrightarrow \exp\left(\frac{E_F^{QC} - E_C}{kT} \right) = \frac{n_D}{2} \left(\frac{2\pi\hbar^2}{m_e^* kT} \right)^{\frac{3}{2}} + \exp\left(\frac{E_F^0 - E_C}{kT} \right), \qquad (5.9)$$

where we have used the relation (5.7). To calculate the Fermi level $E_F^0(T)$, we start with the neutrality condition for a pure semiconductor (5.1), using again (5.7) and (5.8),

$$n_e = n_h$$

$$\Leftrightarrow 2 \left(\frac{m_e^* kT}{2\pi\hbar^2} \right)^{\frac{3}{2}} \exp\left(\frac{E_F^0 - E_C}{kT} \right) = 2 \left(\frac{m_h^* kT}{2\pi\hbar^2} \right)^{\frac{3}{2}} \exp\left(-\frac{E_F^0 - E_V}{kT} \right)$$

$$\Leftrightarrow \qquad \exp\left(\frac{E_F^0 - E_C}{kT} \right) = \left(\frac{m_h^*}{m_e^*} \right)^{\frac{3}{4}} \exp\left(-\frac{\Delta E_g}{2kT} \right) \qquad (5.10)$$

$$\Leftrightarrow \qquad \exp\left(\frac{E_F^0 - E_V}{kT} \right) = \left(\frac{m_h^*}{m_e^*} \right)^{\frac{3}{4}} \exp\left(\frac{\Delta E_g}{2kT} \right). \qquad (5.11)$$

With eq. (5.9) and (5.10) we have

$$\exp\left(\frac{E_F^{QC} - E_C}{kT} \right) = \frac{n_D}{2} \left(\frac{2\pi\hbar^2}{m_e^* kT} \right)^{\frac{3}{2}} + \left(\frac{m_h^*}{m_e^*} \right)^{\frac{3}{4}} \exp\left(-\frac{\Delta E_g}{2kT} \right) \qquad (5.12)$$

$$\Leftrightarrow E_F^{QC} = E_C + kT \ln \left\{ \frac{n_D}{2} \left(\frac{2\pi\hbar^2}{m_e^* kT} \right)^{\frac{3}{2}} + \left(\frac{m_h^*}{m_e^*} \right)^{\frac{3}{4}} \exp\left(-\frac{\Delta E_g}{2kT} \right) \right\} \qquad (5.13)$$

So that for small T the result is equal to neglecting the thermal above-gap excitation

$$E_F^{QC} = E_C - kT \ln \left\{ \frac{2}{n_D} \left(\frac{m_e^* kT}{2\pi\hbar^2} \right)^{\frac{3}{2}} \right\} \qquad (5.14)$$

and for large T it becomes the result of an intrinsic semiconductor (5.10)

$$E_F^{QC} = \frac{E_C + E_V}{2} - \frac{3}{4}kT \ln\left(\frac{m_e^*}{m_h^*}\right).$$ (5.15)

5.2 Holes

For the holes it is a little more complicated because the acceptors are in generally not fully ionized. The thermal average occupancy of the acceptor states is (cf. Kittel and Kroemer, 1980 (p.370) [5])

$$f(A^-) = \frac{1}{1 + 2 \exp\left(\frac{E_A - E_F^{QV}}{kT}\right)} \tag{5.16}$$

$$\Rightarrow f(A^0) = 1 - f(A^-) = \frac{1}{1 + \frac{1}{2} \exp\left(\frac{E_F^{QV} - E_A}{kT}\right)}, \tag{5.17}$$

with E_A the energy level of the acceptor states.

For cryogenic temperatures we would expect the quasi Fermi level of the holes, E_F^{QV}, to be somewhere between E_V and E_A, because at $0\,\mathrm{K}$ all the holes will be in the acceptor states. With higher temperature the acceptor states should ionize and the quasi Fermi level should rise until again thermal excitations between the two bands will arise.

To describe the quasi equilibrium of the holes, we can adjust the neutrality condition (5.2) into

$$n_h = n_A^- = n_A \cdot f(A^-), \tag{5.18}$$

where we again are going to add an extra term for the thermal above-gap excitations. We additionally define for reasons of clarity and comprehensibility

$$c_T := \frac{n_A}{2} \left(\frac{2\pi\hbar^2}{m_h^* kT}\right)^{\frac{3}{2}}$$

$$X_i := \exp\left(\frac{E_i - E_V}{kT}\right).$$

This gives us for the additional term

$$\Rightarrow \frac{1}{V} \int\limits_{-\infty}^{E_V} dE\, \rho_V(E) f_h(E, E_F^0) \overset{(5.8)}{=} 2 \left(\frac{m_h^* kT}{2\pi\hbar^2}\right)^{\frac{3}{2}} \exp\left(\frac{E_V - E_F^0}{kT}\right)$$

$$\overset{(5.11)}{=} \frac{n_A}{c_T} \left(\frac{m_e^*}{m_h^*}\right)^{\frac{3}{4}} \exp\left(-\frac{\Delta E_g}{2kT}\right) = \frac{n_A}{c_T} \frac{(m_e^*/m_h^*)^{\frac{3}{4}}}{\sqrt{X_C}}$$

So, we have with eq. (5.11)

$$n_A \cdot f(A^-) = n_h - \frac{1}{V} \int\limits_{-\infty}^{E_V} dE \, \rho_V(E) f_h(E, E_F^0)$$

$$\Rightarrow \frac{n_A}{1 + 2\frac{X_A}{X_F^{QV}}} = \frac{n_A}{c_T} \frac{1}{X_F^{QV}} - \frac{n_A}{c_T} \frac{(m_e^*/m_h^*)^{\frac{3}{4}}}{\sqrt{X_C}}$$

$$\Leftrightarrow c_T = \frac{1}{X_F^{QV}} + 2\frac{X_A}{\left(X_F^{QV}\right)^2} - \frac{(m_e^*/m_h^*)^{\frac{3}{4}}}{\sqrt{X_C}} \left(1 + 2\frac{X_A}{X_F^{QV}}\right)$$

$$\Leftrightarrow 0 = \left(\frac{X_A}{X_F^{QV}}\right)^2 + \left[\frac{1}{2} - \left(\frac{m_e^*}{m_h^*}\right)^{\frac{3}{4}} \frac{X_A}{\sqrt{X_C}}\right] \frac{X_A}{X_F^{QV}} - \left(\frac{m_e^*}{m_h^*}\right)^{\frac{3}{4}} \frac{X_A}{2\sqrt{X_C}} - \frac{c_T X_A}{2}$$

$$\overset{X_i > 0}{\Leftrightarrow} \frac{X_A}{X_F^{QV}} = \left(\frac{m_e^*}{m_h^*}\right)^{\frac{3}{4}} \frac{X_A}{2\sqrt{X_C}} - \frac{1}{4} + \sqrt{\left[\left(\frac{m_e^*}{m_h^*}\right)^{\frac{3}{4}} \frac{X_A}{2\sqrt{X_C}} + \frac{1}{4}\right]^2 + \frac{c_T X_A}{2}},$$

$$(5.19)$$

where in the last step we have used

$$\left[\left(\frac{m_e^*}{m_h^*}\right)^{\frac{3}{4}} \frac{X_A}{2\sqrt{X_C}} - \frac{1}{4}\right]^2 + \left(\frac{m_e^*}{m_h^*}\right)^{\frac{3}{4}} \frac{X_A}{2\sqrt{X_C}} = \left[\left(\frac{m_e^*}{m_h^*}\right)^{\frac{3}{4}} \frac{X_A}{2\sqrt{X_C}} + \frac{1}{4}\right]^2.$$

Now we can consider different temperature regimes to simplify this equation.

$$\frac{X_A}{\sqrt{X_C}} = \exp\left(-\frac{E_C - E_V}{2kT} + \frac{E_A - E_V}{kT}\right) \approx \exp\left(-\frac{\Delta E_g}{2kT}\right)$$

This term vanishes for $T \to 0$ and becomes relevant for very high temperatures. On the contrary, $c_T \cdot X_A \propto T^{-3/2} \exp[(E_A - E_V)/kT]$ gets relevant for low temperatures and small for high temperatures. But there is also a third regime at intermediate temperature, where one can neglect the $X_A/\sqrt{X_C}$-term while $c_T \cdot X_A \approx c_T$, which is still small because of the $\hbar^3$.

Low temperature:

$$\frac{X_A}{X_F^{QV}} \approx \sqrt{\frac{c_T X_A}{2}}$$

$$\Rightarrow\ E_F^{QV} = \frac{E_A + E_V}{2} + kT \ln\left\{ \frac{2}{\sqrt{n_A}} \left(\frac{m_h^* kT}{2\pi\hbar^2} \right)^{\frac{3}{4}} \right\} \tag{5.20}$$

Intermediate temperature:

$$\frac{X_A}{X_F^{QV}} \approx \frac{1}{4} \left(-1 + \sqrt{1 + 8c_T X_A} \right) \approx c_T X_A$$

$$\Rightarrow\ E_F^{QV} = E_V + kT \ln\left\{ \frac{2}{n_A} \left(\frac{m_h^* kT}{2\pi\hbar^2} \right)^{\frac{3}{2}} \right\} \tag{5.21}$$

High temperature:

$$\frac{X_A}{X_F^{QV}} \approx \left(\frac{m_e^*}{m_h^*} \right)^{\frac{3}{4}} \frac{X_A}{\sqrt{X_C}}$$

$$\Rightarrow\ E_F^{QV} = \frac{E_C + E_V}{2} - \frac{3}{4} kT \ln\left(\frac{m_e^*}{m_h^*} \right) \tag{5.22}$$

The whole temperature dependence of the quasi Fermi levels of both the holes and the electrons are shown in fig. 1. One can now see that in the high temperature regime $E_F^{QV} = E_F^{QC} = E_F^0$ holds true, which is the case in an intrinsic semiconductor. Furthermore, the second regime has exact the same form as the low temperature regime of E_F^{QC} which indicates that in this regime the acceptors are fully ionized. In the supplementary materials for the paper of Saeedi et al. (2013) [3], the authors stated that the percentage of ionized acceptors would be one percent at 30 K and at a temperature of 70 K almost all the acceptors would be ionized. Now, one can see that at 30 K, indeed, one percent of the acceptors are ionized (see fig. 2) and at 70 K only ten percent of neutral donors remain. This small temperature interval is due to the small width of the Fermi distribution, $2kT$, as it passes the energy level of the acceptors.
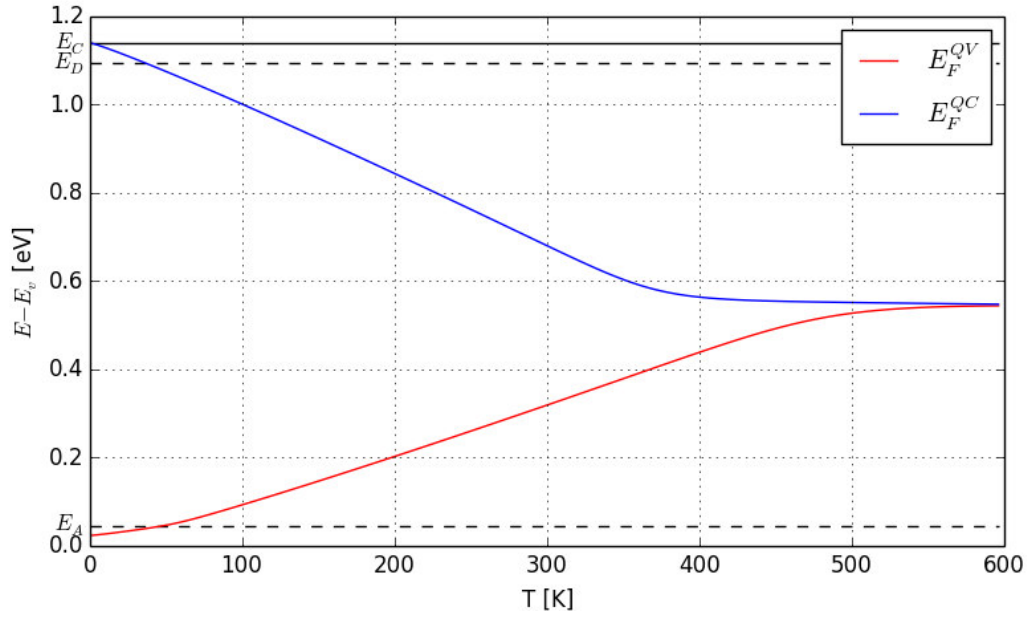
Figure 1 – The quasi Fermi levels of the conduction electrons (*blue*) and the holes (*red*) as a function of temperature.
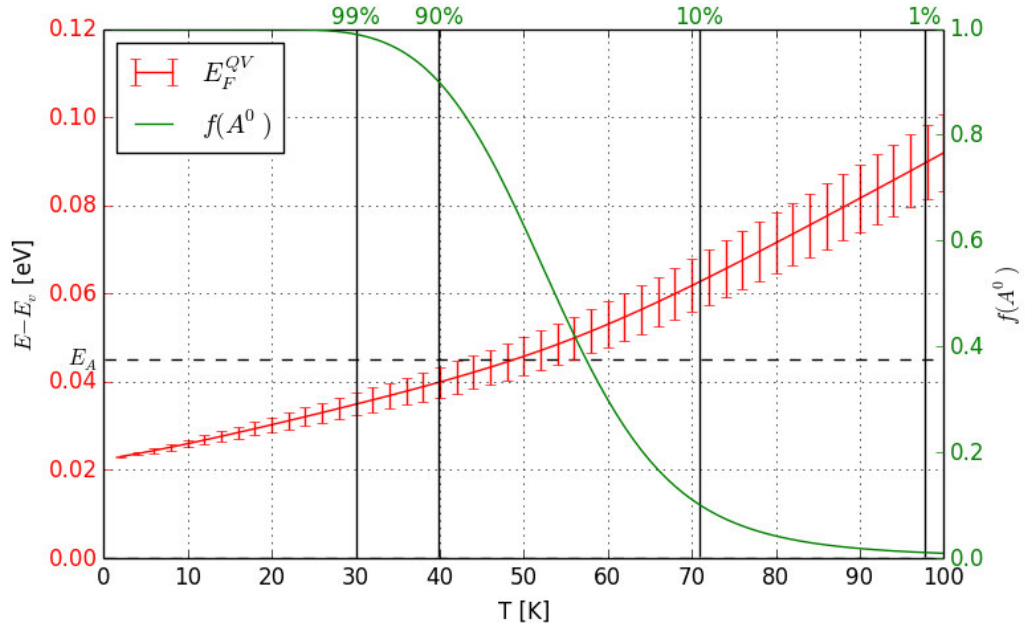

Figure 2 – The quasi Fermi level of the holes (*red*) and the remaining relative amount of neutral acceptors (*green*), both as a function of temperature. The ionization levels of 1%, 10%, 90% and 99% are indicated. The error bars are just $\pm kT$ as a measure for the width of the Fermi distribution.

5.3 Total Equilibrium

So, for high temperatures the quasi Fermi levels will move together and the system can then be described by one Fermi level, as in a total equilibrium. But it is possible that this total equilibrium even occurs at a lower temperature. This would involve that the quasi Fermi levels suddenly jump together, caused by electron-hole recombination. Therefore, we will now consider a total equilibrium. So we start with the neutrality condition for doped semiconductors (5.2):

$$n_e - n_h = n_D^+ - n_A^- \approx n_D - n_A,$$

where we use that the equilibrium only shows up for high temperatures while the acceptors are already fully ionized. For n_e and n_h we again use eq. (5.7) and (5.8). We also use the following definitions

$$\tilde{c}_T := \frac{n_A - n_D}{2} \left(\frac{2\pi\hbar^2}{m_h^* kT} \right)^{\frac{3}{2}}$$

$$X_i := \exp\left(\frac{E_i - E_V}{kT} \right)$$

$$\Rightarrow n_D - n_A = 2 \left(\frac{m_h^* kT}{2\pi\hbar^2} \right)^{\frac{3}{2}} \left[\left(\frac{m_e^*}{m_h^*} \right)^{\frac{3}{2}} \exp\left(\frac{E_F - E_C}{kT} \right) - \exp\left(\frac{E_V - E_F}{kT} \right) \right]$$

$$\Rightarrow 0 = \left(\frac{m_e^*}{m_h^*} \right)^{\frac{3}{2}} \frac{X_F}{X_C} - \frac{1}{X_F} + \tilde{c}_T$$

$$\Leftrightarrow 0 = X_F^{-2} - \tilde{c}_T X_F^{-1} - \left(\frac{m_e^*}{m_h^*} \right)^{\frac{3}{2}} \frac{1}{X_C}$$

$$\overset{X_F > 0}{\Leftrightarrow} \frac{1}{X_F} = \frac{\tilde{c}_T}{2} + \sqrt{ \left(\frac{\tilde{c}_T}{2} \right)^2 + \left(\frac{m_e^*}{m_h^*} \right)^{\frac{3}{2}} \frac{1}{X_C} }$$

So that for high temperatures, we have the intrinsic regime

$$\frac{1}{X_F} \approx \sqrt{ \left(\frac{m_e^*}{m_h^*} \right)^{\frac{3}{2}} \frac{1}{X_C} }$$

$$\Rightarrow E_F = \frac{E_C + E_V}{2} - \frac{3}{4} kT \ln\left(\frac{m_e^*}{m_h^*} \right)$$
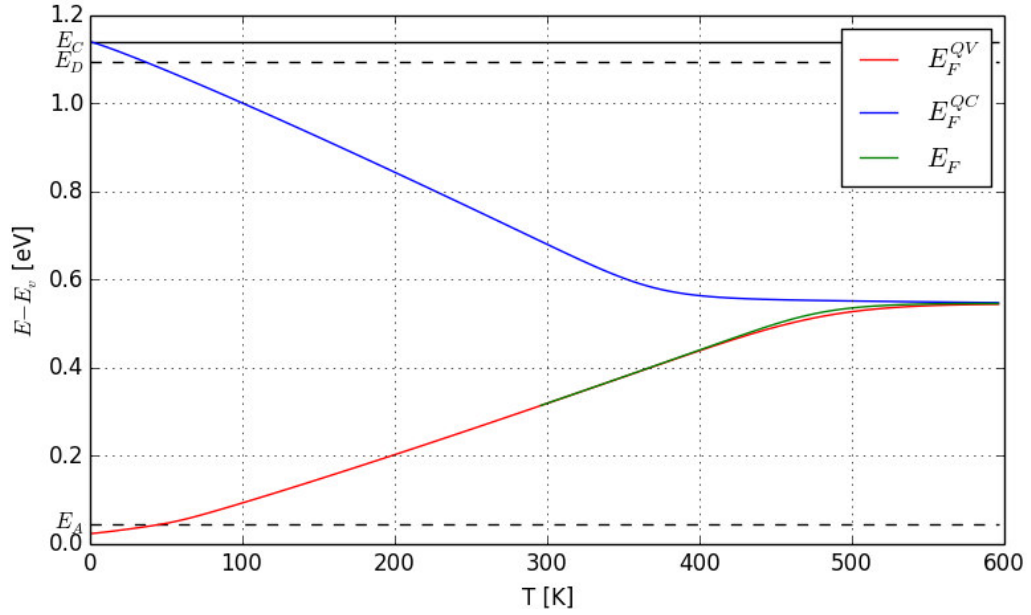
Figure 3 – The quasi Fermi levels in comparison to the Fermi level in a total equilibrium (*green*).

and for intermediate temperatures, since the low-temperature case is excluded because of the full ionization of the acceptor states, we have

$$\frac{1}{X_F} \approx \frac{\tilde{c}_T}{2} + \sqrt{\left(\frac{\tilde{c}_T}{2}\right)^2} = \tilde{c}_T$$
$$\Rightarrow E_F = E_V + kT \ln\left\{ \frac{2}{n_A - n_D} \left(\frac{m_h^* kT}{2\pi\hbar^2}\right)^{\frac{3}{2}} \right\}$$

In fig. 3 one can see that the Fermi level in the total equilibrium varies only very little from the quasi Fermi level of the holes, due to the fact that the concentration of acceptors is by a factor of 100 greater than the concentration of donors.

6 Relaxation Time

Now that we have calculated the Fermi levels, we can continue on calculating the contribution to the relaxation time T_1. So we start with eq. (4.4) using again the Boltzmann distribution (4.9). We also set the energy level of the average of the wave function, $\left\langle |u_{\boldsymbol{k}}(0)|^2 \right\rangle_E^2$, to the respective band edge, because most of the free carriers will be near the band edge, as already discussed earlier. We furthermore use the approximation $f(E)[1 - f(E)] \approx f(E)$, which is a good approximation since we use the Boltzmann distribution. This gives us, using eq (4.6) and (4.7),

$$
\begin{aligned}
G(T) &= \int dE \left\langle |u_{\boldsymbol{k}}(0)|^2 \right\rangle_E^2 \rho^2(E)\, f(E)[1 - f(E)] \\
&= \left\langle |u_{\boldsymbol{k}}(0)|^2 \right\rangle_{E_C}^2 \int\limits_{E_C}^{\infty} dE\, \rho_C^2(E,T) f_e(E,T)[1 - f_e(E,T)] \\
&\quad + \left\langle |u_{\boldsymbol{k}}(0)|^2 \right\rangle_{E_V}^2 \int\limits_{-\infty}^{E_V} dE\, \rho_V^2(E,T) f_h(E,T)[1 - f_h(E,T)] \\
&= \left\langle |u_{\boldsymbol{k}}(0)|^2 \right\rangle_{E_C}^2 \left(\frac{V}{2\pi^2}\right)^2 \left(\frac{2m_e^*}{\hbar^2}\right)^3 \int\limits_{E_C}^{\infty} dE\, (E - E_C) \exp\left(\frac{E_F^{QC} - E}{kT}\right) \\
&\quad + \left\langle |u_{\boldsymbol{k}}(0)|^2 \right\rangle_{E_V}^2 \left(\frac{V}{2\pi^2}\right)^2 \left(\frac{2m_h^*}{\hbar^2}\right)^3 \int\limits_{-\infty}^{E_V} dE\, (E_V - E) \exp\left(\frac{E - E_F^{QV}}{kT}\right).
\end{aligned}
$$

If one approximate the wave function to be constant with respect to the location[7], from the normalization can be followed

$$
1 = \int\limits_{\text{crystal}} |u_{\boldsymbol{k}}(r)|^2\, d^3r \approx |u_{\boldsymbol{k}}(0)|^2 \int\limits_{\text{crystal}} d^3r
$$

$$
\Rightarrow \quad |u_{\boldsymbol{k}}(0)|^2 = \frac{1}{V}
$$

$$
\Rightarrow \left\langle |u_{\boldsymbol{k}}(0)|^2 \right\rangle_E^2 = \frac{1}{V^2}
$$

---

[7]This is maybe a very radical approximation. Actually, the wave function should be much higher at the nucleus ($\boldsymbol{r} = \boldsymbol{0}$) which would lead to a smaller relaxation time, but let us go on with that at the moment.

$$\Rightarrow G(T) = \left(\frac{kT}{2\pi^2}\right)^2 \left(\frac{2m_e^*}{\hbar^2}\right)^3 \exp\left(\frac{E_F^{QC} - E_C}{kT}\right) \underbrace{\int_0^\infty dX \, X \exp(X)}_{\substack{part.\\int. = \int_0^\infty dX \, \exp(X) = 1}}$$

$$+ \left(\frac{kT}{2\pi^2}\right)^2 \left(\frac{2m_h^*}{\hbar^2}\right)^3 \exp\left(-\frac{E_F^{QV} - E_V}{kT}\right) \underbrace{\int_0^\infty dX \, X \exp(X)}_{=1}$$

$$\overset{(4.5)}{\Rightarrow} \frac{1}{T_1} = \frac{4}{9}\pi\hbar^3 \mu_0^2 \gamma_e^2 \gamma_n^2 \cdot G(T)$$

$$= \frac{8}{9} \frac{(\mu_0 \gamma_e \gamma_n kT)^2}{\pi^3 \hbar^3} \left[m_e^{*3} \exp\left(\frac{E_F^{QC} - E_C}{kT}\right) + m_h^{*3} \exp\left(\frac{E_V - E_F^{QV}}{kT}\right) \right]$$

Now, we can either plug in the quasi Fermi levels, (5.12) and (5.19), or the Fermi level for the total equilibrium and calculate the relaxation time for a given temperature. The value for the band gap of silicon, $\Delta E_g = E_V - E_C = 1.14\,\text{eV}$, and the effective masses for silicon in units of the free electron mass, $m_e^* = 1.06 \cdot m_e$ and $m_h^* = 0.58 \cdot m_e$, were taken from table 13.1 (p.357) of the book of Kittel and Kroemer (1980) [5]. From table 13.2 (p.368) of the same book were taken the ionization energies of phosphorus and boron in silicon, $E_C - E_D^{(P)} = E_A^{(B)} - E_V = 45\,\text{meV}$. With this we obtain

$$T_1(289K) \approx 200\,\text{years} \qquad\qquad \text{in total equilibrium,}$$
$$T_1(289K) \approx 194\,\text{years} \qquad\qquad \text{in quasi equilibrium,}$$
$$T_1(1.9K) \approx 100{,}600\,\text{years.}$$

7 Conclusion

The received relaxation times are obviously much larger than the measured results from the experiment. This means that we can not explain the experimental results with this calculations and this leads to the assumption that the contribution delivered by the considered mechanism is too small. We would probably obtain a better result if we had a better approach on the wave function at the nucleus, but it is highly doubtful whether this explains the results on its own. So, there has to be other interactions which cause relaxation, e.g. interaction between the nuclei and the phonons of the lattice.

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