Simulation of TF-µSR histograms in germanium in the presence of cyclic charge state transitions of muonium

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Abstract. It has recently been shown that at T < 270 K a persistent inversion from n- to p-type can be induced by illumination in a 200-nm-thick surface layer of lowly-doped commercial germanium wafers [1]. The presence of photo-generated holes is detected by the appearance of a fast relaxing component in TF-µSR measurements, caused by cyclic muonium charge state transitions Mu\(^-\)_T + h\(^+\) ⇔ Mu\(^0\)_T. For a quantitative determination of the photo-induced hole carrier concentration we use a Monte-Carlo simulation to generate muon decay histograms for different hole capture rates (forward reaction), and ionization rates (reverse reaction due to thermal activation) [2]. The hole carrier concentration is determined by comparing simulated and experimental relaxation rates. These results have been used to estimate the photo-induced hole concentration in low-energy µSR experiments [1].

1. Introduction

In semiconductors the presence of free charge carriers can give rise to charge state transitions of muonium. The change of the charged diamagnetic state (either Mu\(^+\) or Mu\(^-\)) to the neutral paramagnetic state Mu\(^0\) causes a loss of muon spin phase coherence due to the hyperfine interaction in Mu\(^0\), which can be the origin of the appearance of a fast relaxing component in either longitudinal (LF) or transverse field (TF) µSR experiments. Recently, a photo-induced persistent inversion from n- to p-type of a hundreds of nanometer thick surface layer of commercial germanium wafers has been observed by low-energy TF-µSR at temperatures T < 270 K [1]. Here, the photo-generated holes become noticeable by the occurrence of a fast relaxing component in the diamagnetic precession signal. In view of a potential application of this effect to device technology it is important to know the photo-generated hole carrier concentration p. This question has motivated the current study, where we will show that p can be determined from the observed fast relaxation rate \(\Lambda_f\) of the diamagnetic signal by means of a Monte-Carlo technique [2].

In germanium, at T > 180 K, the thermally activated ionization of Mu\(^0\)_T (muonium at the tetrahedral interstitial site) to the Mu\(^-\)_T state leads to an increase of the diamagnetic asymmetry as a function of temperature [3]. In the presence of free holes h\(^+\) cyclic charge state transitions Mu\(^-\)_T + h\(^+\) = Mu\(^0\)_T cause a fast relaxing component of the diamagnetic µSR asymmetry, where the fast relaxation rate \(\Lambda_f\) depends on p. The ionization of Mu\(^0\)_T can be well described by an Arrhenius rate process with an ionization rate \(\Lambda_i = \Lambda_0 \exp(-E_A/k_BT)\), where \(\Lambda_0\) is the attempt...
frequency, and $E_A$ the activation energy. In germanium $E_A = 170$ meV and $\Lambda_0 = 6.7 \times 10^{13}/s$ were determined in previous bulk $\mu$SR studies [4]. The hole capture rate $\Lambda_c$ is related to $p$ by $\Lambda_c = p \cdot v_p \cdot \sigma_c^h$, where $v_p$ is the temperature dependent hole velocity ($\sim 1.9 \times 10^7$ cm/s at room temperature, $v_p \propto \sqrt{T}$), and $\sigma_c^h$ is the hole capture cross section of Mu$_0^+$, which is expected to be in the order of “typical” atomic cross sections of $10^{-14} - 10^{-15}$ cm$^2$, and which has a temperature dependence $\sigma_c^h \propto T^{-2}$ [4]. We will show in section 2 that the TF-$\mu$SR $\Lambda_f \propto \Lambda_c$, and therefore $\Lambda_f \propto p$.

In LF-$\mu$SR experiments the longitudinal muon spin $1/T_1$ relaxation in muonium undergoing cyclic charge exchange can be expressed as [4, 5, 6]

$$1/T_1 = 0.5 \cdot \frac{\Lambda_1 \Lambda_c}{\Lambda_1 + \Lambda_c} \cdot \frac{\omega_0^2}{\omega_0^2 + \omega_p^2(1 + x^2)},$$

where $\omega_0 = 2\pi \cdot 2359.5$ MHz is the hyperfine coupling of Mu$_0^+$, and $x = B/B_0$ with $B_0 = \omega_0/(\gamma_\mu - \gamma_e) = 0.0839$ T. Knowing $E_A$ and $\Lambda_0$ allows to calculate $\Lambda_1$ as a function of temperature. Thus, Eq. 1 contains only $\Lambda_c$ as an unknown parameter, which can be determined by fitting Eq. 1 to $1/T_1$ data measured as a function of magnetic field and temperature. Therefore, it appears to be more appropriate to do LF-$\mu$SR $1/T_1$ measurements rather than TF-$\mu$SR to determine $\Lambda_c \propto p$. However, this approach only works if $p$ is constant during the field and temperature scans. This is not the case for the experiments of Ref. [1] showing the photo-induced persistent inversion, where illumination was carried out for some time (minutes to hours) at 220 K, followed by persistent inversion, where illumination was carried out for some time (minutes to hours) at 220 K and higher temperatures, where holes disappeared by recombination due to the finite lifetime of the photo-induced inversion. Moreover, the temperature and field scans are a time consuming procedure, whereas our aim is to determine $p$ in the end by a single TF-$\mu$SR measurement. In the following section we will describe the method how this can be achieved.

2. Simulation procedure and results

We use a Monte-Carlo simulation [2] to calculate the evolution of the muon spin phase in an applied magnetic field in the presence of the cyclic charge state transitions described in the previous section. The ionization of Mu$_0^+$ with its effect on the diamagnetic signal is simulated the following way (assuming $p = 0$, i.e. hole capture is neglected):

- at time $t = 0$, the muon is in the Mu$_0^+$ state with a probability of 100%. Its decay time $t_d$ is “thrown” according to the exponential muon decay probability $\exp(-t/\tau_\mu)$ ($\tau_\mu$ the muon life time).
- for a given applied transverse magnetic field four precession (“transition”) frequencies $\nu_{ij}$ are possible, see the Breit-Rabi diagram in Fig. 1. The probabilities $a_{ij}$ for the precession frequencies $\nu_{ij}$ are field dependent, with $a_{12} = a_{34}$ and $a_{23} = a_{14}$.
- according to the probabilities $a_{ij}$ the simulation “throws” one of the four precession frequencies. Transition frequencies and probabilities for the experimentally applied field of 0.1 T are shown in Tab. 1.
- the time of ionization $t_i$ is “thrown” according to the ionization rate $\Lambda_i$.
- if $t_i > t_d$, the muon precesses with frequency $\nu_{ij}$ until it decays, and the muon spin phase (precession angle) is $\Phi(t_d) = 2\pi \nu_{ij} t_d$. If $t_i < t_d$ the muon precesses with $\nu_{ij}$ until $t_i$, and after ionization the muon precesses now with its Larmor frequency $\nu_\mu$ until it decays. In this case we get $\Phi(t_d) = 2\pi \nu_{ij} t_i + 2\pi \nu_\mu (t_d - t_i)$. The decay positron histogram at time bin $t_d$ is incremented by $1 + A \cdot \cos[\Phi(t_d)]$, where $A$ is the muon decay asymmetry.

For increasing temperature the ionization rate $\Lambda_i$ increases exponentially and once $\Lambda_i \gtrsim \nu_{ij}$ the lifetime of Mu$_0^+$ is short enough so that the dephasing of the muon spin in the hyperfine field
Table 1. Transition frequencies and probabilities of isotropic Mu\textsubscript{T\textsuperscript{0}} in germanium in an applied transverse field of 0.1 T.

| transition | frequency (MHz) | probability |
|------------|-----------------|-------------|
| \(\nu_{12}\) | 736.9 | 0.441 |
| \(\nu_{34}\) | -1622.6 | 0.441 |
| \(\nu_{23}\) | 2048.8 | 0.059 |
| \(\nu_{14}\) | 4408.3 | 0.059 |

of the electron becomes sufficiently small: a coherent precession at the Larmor frequency \(\nu_{\mu}\) occurs, and the diamagnetic asymmetry \(A_D\) of muons precessing at \(\nu_{\mu}\) increases as the lifetime of Mu\textsubscript{T\textsuperscript{0}} decreases. An increase of \(A_D\) as a function of temperature is the result, as can be seen in Fig. 2, which shows excellent agreement between simulation and experimental data for the proper choice of \(E_A\).

Hole capture of Mu\textsubscript{T\textsuperscript{-}} at a rate \(\Lambda_c\) leads to a depolarization of the diamagnetic signal, if the lifetime of the generated Mu\textsubscript{T\textsuperscript{0}} state is long enough to cause dephasing of the diamagnetic fraction. In the presence of holes the simulation uses \(\Lambda_i\) and \(\Lambda_c\) as input parameters, and “throws” the times \(t_{i,c}\) of successive ionization/capture processes, and follows the muon spin phase in the different charge states with precession frequencies \(\nu_{ij}\) and \(\nu_{\mu}\), until the muon decays. For each Mu\textsubscript{T\textsuperscript{0}} a different transition \(\nu_{ij}\) may occur according to the transition probabilities \(a_{ij}\).

Figure 1. Breit-Rabi diagram with possible transitions \(\nu_{ij}\) in a transverse magnetic field \(B\) of isotropic muonium Mu\textsubscript{T\textsuperscript{0}} in Ge with a hyperfine coupling of 2359.5 MHz.

Figure 2. Temperature dependence of the TF-\(\mu\)SR diamagnetic asymmetry \(A_D\) (due to Mu\textsubscript{T\textsuperscript{0}} formation at \(T > 180\) K), comparison of experimental bulk data (GPS, 0.1 T) of nominally undoped n-Ge (100) with simulation data for two different values of \(E_A\): 170 meV (from Ref. [4]), and a lower \(E_A\), which is far off the experimental data between 200 K and 260 K. The maximum diamagnetic asymmetry is 0.21.
In order to test the simulation in the presence of hole capture we used a p-type Ge wafer with $p \sim 10^{15} \text{ cm}^{-3}$, where we determined $\Lambda_c(T)$ and $E_A$ for a fixed $\Lambda_0 = 6.7 \times 10^{13}/s$ by the temperature and $B$-field dependence of $1/T_1$ in bulk LF-$\mu$SR measurements. The data and a global fit according to Eq. 1 are shown in Fig. 3. The obtained value for $E_A$ is in good agreement with the 170 meV from previous bulk studies [4]. In [4] the hole capture cross section has been found to decrease with temperature as $T^{-2}$. Here, we find $\Lambda_c \propto T^{-2.4(2)}$, which means – assuming that $p$ is constant in the temperature range of the experiment – that $v_p \cdot \sigma_c^h \propto T^{-2.4(2)}$. For the usual temperature dependence $v_p \propto \sqrt{T}$ one would expect a weaker temperature dependence $v_p \cdot \sigma_c^h \propto T^{-3/2}$. On the other hand the mobility of holes in germanium scales as $T^{-2.5}$ [7] and this suggests that the temperature dependence of $\Lambda_c$ is governed by the hole carrier mobility. For the Monte-Carlo simulations of the TF-$\mu$SR histograms we use the temperature dependence determined by the LF-$\mu$SR measurements. The TF-$\mu$SR fast relaxation rates as a function of temperature are shown in Fig. 4. Below 260 K the fast relaxation rate is too high ($\Lambda_f > 100 \mu s^{-1}$) to be reliably fitted. The blue squares are the $\Lambda_f$ from the simulation, where the $\Lambda_c(T)$ are specified for each temperature: there is excellent agreement within errors between simulation and experiment. At 270 K two additional simulated fast relaxation rates for $\Lambda_c = 200$ and $\Lambda_c = 300$ MHz are displayed for comparison. They demonstrate that $\Lambda_f \propto \Lambda_c$, and therefore $\Lambda_f \propto p$ for a given temperature.

We now turn to the low-energy $\mu$SR illumination data of nominally undoped $n$-Ge from two different suppliers (Crystec GmbH and MTI corporation) [1]. The relaxation rates as a function of temperature and illumination are shown in Fig. 5. In the dark, only a slowly relaxing diamagnetic component with relaxation rate $\Lambda_s$ is observable. When turning on the light at 220 K the fast relaxing component with rate $\Lambda_f$ appears, which is revealing of the appearance of holes. Even after turning off the light at 220 K and slowly warming up, the fast component – i.e. the photo-generated holes – persists up to a temperature of $\sim 270$ K, where the hole carriers quickly disappear, indicated by the fast drop of $\Lambda_f$. This persistent hole accumulation has its origin in the trapping of photo-generated electrons in empty surface acceptor states. The negatively charged surface keeps the holes in the at least 200-nm-thick
Crystec, no light
Crystec, 3h, white, 10mW/cm²
Crystec, 5h, white, 10mW/cm²
MTI, 2h, λ=470nm, 10mW/cm²
MTI, 50min, λ=405nm, 80mW/cm²

Figure 5. TF-µSR relaxation rates $\Lambda_s$ and $\Lambda_f$ of the slowly and fast relaxing components as a function of temperature $T$ and illumination history for two different commercial wafers (Crystec and MTI), low-energy µSR data at a mean depth $\langle z \rangle = 85$ nm, $B = 0.1$ T. Without the presence of holes there is only a slowly relaxing component visible: the $\Lambda_s$ data beneath the purple line. Symbols: experimental data from [1]. Solid and dashed lines: simulation results for different hole capture rates.

surface layer. Only after warming to $T > 270$ K, the trapped electrons are released from the surface acceptor states to recombine with the holes. The solid lines illustrate the results of the simulation for fixed (temperature independent) hole capture rates $\Lambda_c$. The decrease of $\Lambda_f(T)$ is caused in this case by the exponentially increasing ionization rate of Mu$_0^T$, which means that the muon spends less and less time in the neutral state, thus reducing the phase decoherence, i.e. $\Lambda_f$. The dashed line uses the $T^{-2.4}$ dependence of $\Lambda_c$ determined in the LF-µSR measurement. Here, $\Lambda_f(T)$ is decreasing faster compared to the fixed $\Lambda_c$ data because of the decreasing hole capture rate.

We now use the 240 K data to quantitatively estimate the photo-induced hole carrier concentration $p_{pi}$. According to Fig. 5 one needs $\Lambda_c(240K)$ to be between $150 \times 10^6$/s and $200 \times 10^6$/s to obtain the experimental value of $\Lambda_f$. Using the $p \sim 10^{15}$ cm$^{-3}$ sample as reference with $\Lambda_c^{15}(240K) = 1230 \times 10^6$/s, we obtain $p_{pi} = 200/1230 \times 10^{15}$ cm$^{-3} = 1.6 \times 10^{14}$ cm$^{-3}$, which is in excellent agreement with estimates from resistance measurements [1].

3. Discussion and summary
In ultra-pure germanium in Ref. [4] a different charge transition for Mu$_0^T$ was suggested, involving a change to the bond-centred (BC) site: Mu$_0^T$ $\rightleftharpoons$ Mu$_{BC}^++e^-$. In a recent study [8] on silicon-germanium alloys the formation of Mu$_T$ has been suggested to result from the process Mu$_0^T$ $\rightarrow$ Mu$_{BC}^0$ $\rightarrow$ Mu$_T^-$. However, these assignments do not naturally explain the observed effects in the presence of holes in the ionization region at $T > 200$ K in TF-µSR data (in particular the conversion of Mu$_0^T$ to Mu$_{BC}^0$ does not explain how Mu$_{BC}^0$ retransforms to Mu$_0^T$ in the presence of holes), nor do they represent the most simple model for the charge cycles in the
p-type sample LF-µSR measurements of Fig 3: the simplest charge cycle to interpret these data is the aforementioned Mu⁻ + h⁺ ⇌ Mu⁰. The temperature dependence of the carrier capture rate of $T^{-2.4(2)}$ also indicates the significance of holes, if one assumes that the carrier capture rate is governed by the carrier mobility: the electron mobility in Ge scales with $T^{-1.7}$, whereas the hole mobility scales with $T^{-2.3}$ [7], in agreement with the present data. In p-type samples with $p$ ranging between $10^{15}$ cm$^{-3}$ and $10^{16}$ cm$^{-3}$ we observe with low-energy muons a depletion of holes at depths of several hundred nanometer (for $p = 10^{15}$ cm$^{-3}$) and tens of nanometer (for $p = 10^{16}$ cm$^{-3}$) [9]. Under illumination – which removes the depletion layer, i.e. holes are moving towards the surface – we observe the appearance of fast relaxing components in LF- and TF-µSR measurements. This further supports the interpretation that the data can be described by charge-cycles involving only holes. In the end the essential result for this work is that the observed data can be described by simple cyclic transitions between two muonium charge states, where the charge capture rate (formation of the neutral state) is governed by the hole carrier concentration, and the formation of the charged state can be described by an Arrhenius like process. The details of the formation of the muonium states – either with or without site change – are less important for the objective of this work, which is the determination of the hole carrier concentration.

In summary we have shown that – in the presence of cyclic muonium charge state transitions – the extrinsic hole carrier concentration in germanium can be estimated by comparing TF-µSR relaxation rates with rates obtained from a Monte-Carlo simulation and by comparison with a reference sample. This is useful for low-energy µSR applications where the charge carrier concentration can be tuned by illumination and/or by electric fields at a semiconductor surface or interface. By means of the Monte-Carlo simulation it is possible to determine the charge carrier concentration by a single TF-µSR measurement, rather than by performing time consuming LF-µSR magnetic field and temperature scans.

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