Muonium reaction in semiconductors and insulators: The role of the transition state

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Muonium reaction in semiconductors and insulators: The role of the transition state

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Abstract. A general scheme for the reaction of muonium with the host lattice of semiconductors and insulators is derived. We begin our considerations when the muonium has been slowed down to a kinetic energy of one to a few eV, an energy at which electron excitations across the band gap are no longer possible and the subsequent deceleration is due to elastic or inelastic processes. Elastic scattering causes energy loss in small portions, on the order of 1 ‰ of kinetic energy per scattering, and eventually leads to atomic muonium at an interstitial site. At these low energies, however, the muonium may stay at one site long enough, especially at the top of the diffusion barrier, to excite a local vibration of the nearest lattice atoms, e.g., a stretching or breathing mode, leading to the stopping of muonium. The configuration formed after the excitation of the local phonon is designated "transition state". This state may exist for some time and may be seen in μSR as a fast relaxing diamagnetic signal. The decay of the transition state may lead either to interstitial atomic muonium or to a bound configuration in the neutral or positive charge state. In the present paper we apply this model to Al_2O_3 and to a Ge-rich SiGe alloy.

1. Introduction

The "transition state" model describes the reaction of atom-like muonium with the host lattice at the end of the implantation trajectory [1, 2, 3, 4, 5, 6]. Reactions of the bare muon (μ^+) with the host are not covered by this model and can be considered as a temperature-independent "background". At the end of the trajectory, the muonium has just enough kinetic energy to jump across the potential barrier from one interstitial site to the next [6]. At the top of the barrier, muonium is so slow that a strong inelastic interaction, e.g., the excitation of a local stretching or breathing mode, can occur and a metastable muon-electron configuration, the transition state, is formed (see Fig. 1).

The decay of the transition state occurs either towards the interstitial site, where atomic muonium (e.g., Mu^0_T) is formed, or towards the bound site (e.g., Mu^0_{BC} or ionized), where the muon is incorporated into the bond structure of the host.

If the lifetime of the transition state is sufficiently long, it can be observed as a fast relaxing diamagnetic signal [6, 7, 8]. Depending on the relative height of the two barriers in Fig. 1, the decay may be dominant in the direction of the interstitial or in the direction of the bound site.

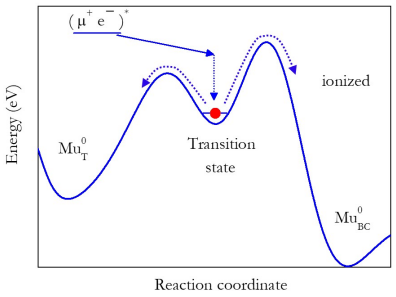

Figure 1. Muonium is trapped at a shallow minimum (transition state) at the top of the diffusion barrier. From there, it can decay thermally activated either to the muonium ground state (e.g. Mu_T^0) or to a bound configuration (e.g. Mu_{BC}^0 or ionized).

The inelastic process leading to the formation of the transition state locally deposits an energy on the order of a few 10 meV to 100 meV, mimicking a short-time temperature rise ("thermal spike") [3].

In the present contribution, the transition state model is applied to Al_2O_3 [6] and to a Ge-rich SiGe alloy [9].

2. Transition state model

We separate the formation of the transition state and its decay and describe them as activated processes across barriers. In the present simple version of the model only integral fractions are considered, fluctuations and dephasing effects have to be added in a more complete model.

2.1. Formation of the transition state

The formation of the transition state at the top of the diffusion barrier competes with the return of muonium to the interstitial site, where it then forms atomic muonium (mostly not observable because of depolarization). The probability of the formation of the transition state depends on various parameters, e.g., on the coupling of the muonium electron with the corresponding phonon, but also on the duration of the interaction. We summarize these different processes by assuming an activated process with activation energy E_0. We set for the transition state fraction f_{tr}:

$$f_{tr} = f_{tr}^0 \exp\left(-\frac{E_0}{k_B T}\right) \tag{1}$$

If no activation is required ($E_0 = 0$), a constant temperature-independent fraction is obtained. This is the case for Al_2O_3, discussed below. But it is also possible that the formation of the transition state requires activation, causing that the transition state is seen only at elevated temperatures. However, the activation energy may be provided by the stopping process itself. In this case, the transition state becomes visible also at low temperatures ("thermal spike" effect) [3]. This case is discussed on the SiGe alloy.

2.2. Decay of the transition state

The decay of the transition state is described by reaction rates ν_i ($i = 1$ for the decay to the interstitial site and $i = 2$ for the decay to the bound site). The inverse lifetime of the transition state $1/\tau$ is the sum of these two rates:

$$\frac{1}{\tau} = \nu_{tr} = \nu_1 + \nu_2 = \nu_0 \left[N_1 \exp\left(-\frac{E_1}{k_B T}\right) + N_2 \exp\left(-\frac{E_2}{k_B T}\right)\right] \tag{2}$$

E_1 and E_2 are the activation energies, N_1 and N_2 are the statistical weight factors reflecting the multiplicity of the reaction possibilities and ν_0 is a common attempt frequency.

The branching between the pathways to the interstitial or bound configuration is given by the ratio of the two reaction rates:

$$\frac{f_1}{f_2} = \frac{\nu_1}{\nu_2} = \frac{N_1}{N_2} \exp\left(-\frac{E_1 - E_2}{k_B T}\right) \tag{3}$$

3. Application of the model to experimental data

3.1. Al_2O_3

In Al_2O_3, a constant diamagnetic fraction of about 6% and a muonium fraction of about 10% are observed at all temperatures (Fig. 2 a)) [6, 10]. However, the dominant fraction is a fast-relaxing component at the muon Larmor frequency which we assign to the transition state.

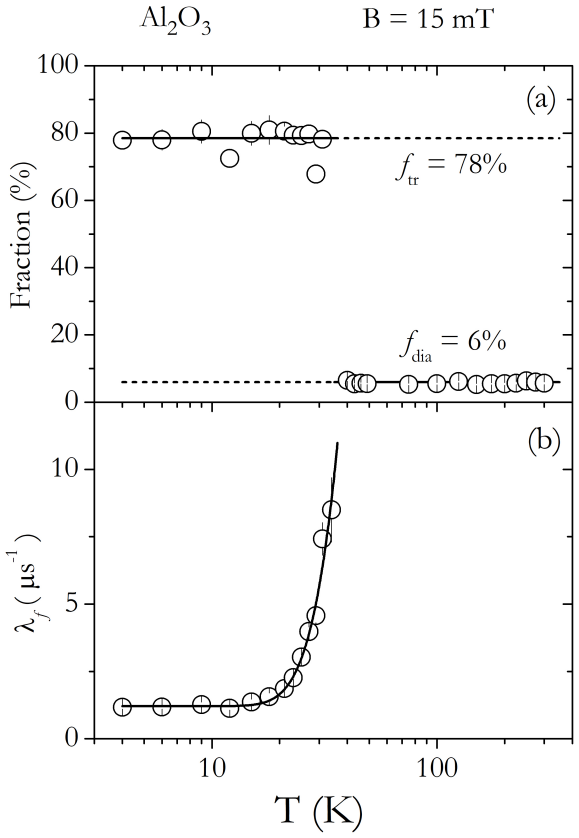

Figure 2. a) Diamagnetic fraction f_{dia} and fast relaxing fraction f_{fast} observed in transverse field experiments on Al_2O_3 [6]. The dashed lines are extrapolations of the measured data. In addition an atomic muonium fraction of about 10% is reported in Ref. [10]. b) Relaxation rate λ_{fast} of the fast relaxing signal. The solid curve is a fit with an activated process ($E_a = 11(1)$ meV).

In the transverse field experiment [6], the fast component is seen only up to about 40 K; at higher temperatures, the large relaxation (Fig. 2 b)) makes observation impossible. However, the signal was seen in a zero-field experiment up to room temperature [11].

Figure 3 shows schematically the potential energy surface along the reaction path of muonium from the interstitial site to the transition state and from there to the ionized configuration. The first part of the potential curve corresponds to the minimum energy path determined in DFT calculations. To the right of the figure, a high barrier towards ionization is indicated. A high barrier against ionization is suggested since DFT calculations show that the 0/+ conversion level lies deep in the gap [6].

Thus, in the Al_2O_3 case, the transition state will decay exclusively to the interstitial muonium configuration. The barrier height for the decay to atomic muonium is derived from the increase of the relaxation rate (interpreted as inverse lifetime) in Fig. 2 b) and amounts to 11 (1) meV.

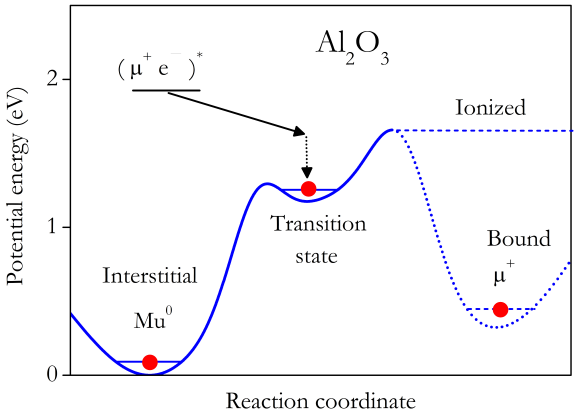

Figure 3. Suggested potential energy surface along the reaction path of muonium from the interstitial site to the transition state and from there to the ionized configuration (based on the results of DFT calculations [6]).

3.2. Electric field experiment by J. D. Brewer et al. [12]
In the experiment of J.D. Brewer *et al.* [12], an externally applied electrical field caused a strong reduction of the fast relaxing diamagnetic fraction in Al_2O_3. An obvious interpretation seemed to be that the signal is due to Mu^- and that the electrical field inhibits the formation of Mu^-, or Mu^- is ionized in the electrical field. In the transition state model, the effect is explained by assuming that the electric field lowers the barrier for the decay of the transition state to interstitial muonium (see Fig.3) and that therefore the fast relaxing (transition state) signal is reduced.

3.3. Ge-rich SiGe alloy
Mengyan *et al.* [9] studied Ge-rich SiGe alloys with the longitudinal-field μSR method. The authors distinguish three differently relaxing signals: fast, intermediate and slow. Their results for the $Si_{0.09}Ge_{0.91}$ alloy are displayed in Fig. 4. We note that in this case the fast component is not constant but needs an activation (Eq. 1). We discuss these data in two steps: a) the low-temperature part below about 70 K which we assign to a thermal spike and b) the interpretation of the three fractions above 70 K.

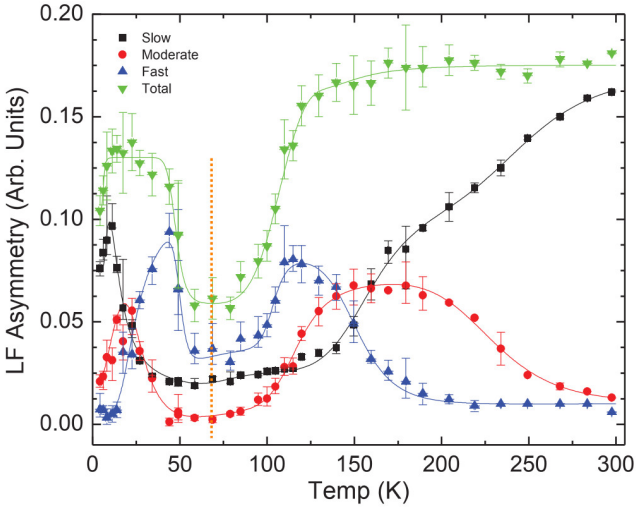

Figure 4. Longitudinal-field (B = 0.07 T) data for $Si_{0.09}Ge_{0.91}$ from P.W. Mengyan *et al.* [9]. Three differently relaxing components are observed: slow (nominally non-relaxing, black), moderate (1–5 μs^{-1}, red), and fast (10 – 30 μs^{-1}, blue). The lines are guide to the eye only. The yellow line has been added by us.

a) Thermal spike. The data below about 70 K look like the mirror image of the data above that temperature, with a compressed temperature scale. We suspect that the release of energy when the muon stops acts like a thermal spike, mimicking the situation at higher temperatures.

Initially, the stopping energy is distributed to a few atoms around the muonium and remains there for some time at low temperature. As the temperature increases, the stopping energy diffuses into the surroundings and the thermal spike effect disappears.

b) Interpretation of the three components (see Fig.5). The sum of the three fractions (total), the green curve in Fig. 5, corresponds to the formation of the transition state. It obviously needs activation (Eq. 1), as shown by the increase of the total fraction above about 100 K. The three curves: blue, red, and black, are assigned to the three decay modes of the transition state. We discuss them in terms of the potential diagram shown in the insert to Fig.5: With increasing temperature, the transition state decays fist in the Mu^0_T direction because the barrier for this process is lower than the barrier to decay in the Mu^0_{BC} direction. However, as the temperature increases further, the higher statistical weight ($N2/N1$ in Eq. 3) of the decay to the bound direction comes into play and the decay to Mu^0_{BC} and ionization increases. Whether Mu^0_{BC} is really formed or whether muonium ionizes before the ground state is reached cannot be decided from these data.

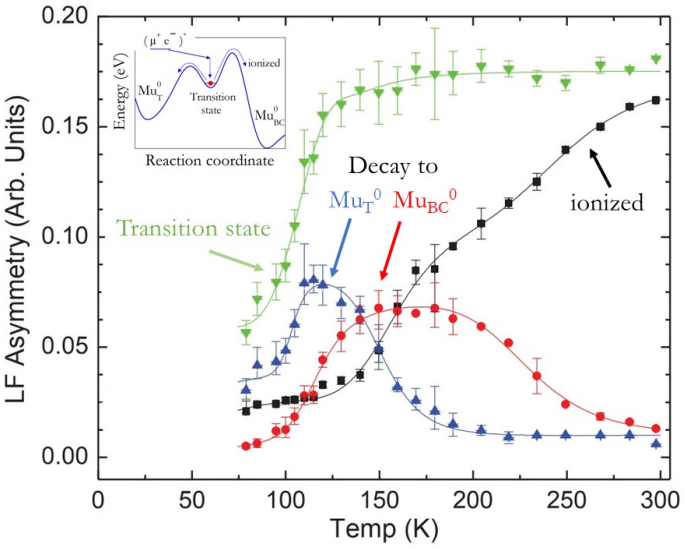

Figure 5. Interpretation of the data of Mengyan *et al.* [9] in the transition state model. The lines are guide to the eye only. The insert shows the suggested potential for the decay of the transition state to Mu^0_T or to Mu^0_{BC} and ionization. Only the data above 70 K are shown for clarity.

4. Conclusions

The present model describes the embedding of muonium into the crystal structure of semiconductors and insulators. A particular point is the formation of an intermediate configuration (transition state) due to the excitation of a local vibration (e.g. a stretching or breathing mode) at the end of the implantation trajectory. The transition state may decay either to the interstitial side forming atomic muonium or to the bound side forming bound muonium or being ionized.

In the present simple version of the model, only integral fractions have been considered. Fluctuations of the configuration and charge and spin exchange with charge carriers have not been included but can be added to the model where appropriate. The inclusion of configuration fluctuations and spin and charge exchange are particularly important when doping or light induced effects are investigated.

Acknowledgments

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