Reply to "Comment on 'Role of the transition state in muon implantation' and 'Thermal spike in muon implantation'"

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The transition state model proposed for muonium formation in solids is critically discussed with respect to the delayed capture model. The two models differ mainly in how the electron capture at the muon is treated. In the delayed capture model the electron stems from the ionization track of the implanted muon. Important electron mobility information is derived in several papers from the time the electron needs to arrive at the muon. In our transition state model, the electron is picked up in the charge-exchange regime during slowing down and is present already when the muon stops in the target. Thus, no information about electron mobility can be obtained from such measurements.

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The authors of the Comment present their "delayed capture" model (delayed muonium formation) and criticize our alternative explanation of the data in the "transition state" concept [1]. The two models differ mainly in how the electron capture at the muon is treated.

In the delayed capture model, the electron stems from the ionization track of the implanted muon and arrives delayed in the region where the positive muon has stopped. Electron mobility data are derived (references in the Comment) from the time the electron needs to arrive at the muon.

In our transition state model, the electron is picked up in the charge-exchange regime and arrives together with the muon at the stopping site. In case of the fast relaxing diamagneticlike signal (more details later) the presence of the electron already at the beginning of the μSR measurement is evidenced by the observed frequency shift. Thus, no mobility data can be obtained from such measurement.

The first part of the Comment is concerned with experiments on cryocrystals and cryoliquids. We have not applied our model to these data; thus, no detailed discussion of these experiments in the transition state model can be presented here. However, we would like to make some critical comments on the delayed capture model in this context. A prerequisite for the applicability of the delayed capture concept is that the muon has not picked up an electron already in the charge-exchange regime. However, e.g., for nitrogen and argon, the main fraction after charge exchange corresponds to neutral muonium (Ref. [2] for the gas phase and Ref. [3] for the solid phase) and the remaining fraction of μ^+ is too small to account for the strength of the signal assigned to the delayed capture process. Moreover, the measuring method based on the delayed capture model is uncritically applied in all cases without checking the conditions for the applicability. The method was not adequate, e.g., in the Al_2O_3 case [4], as will be discussed below in this Reply.

The main part of the Comment refers to "a wide variety of insulators and semiconductors, such as SiO_2, NaCl, Si, GaAs, GaP, and CdS." Specifically discussed is the case of Al_2O_3 for which different interpretations of the fast relaxing μSR signal have been forwarded. In a first paper [4] this signal is assigned to μ^+ which after some delay ($\approx$1 μs) captures an electron from the ionization track. In a later paper with partially overlapping authorship [5], the signal is, on the basis of electrical-field measurements, assigned to Mu^-. In this interpretation, Mu^- is formed promptly (subnanosecond range) and lives for about 1 μs before it loses an electron.

This somewhat unusual Mu^- assignment is defended in the present Comment by (i) "an anomalously high density of highly mobile radiolysis electrons at low temperature" for explaining the prompt capture of two electrons and (ii) the relatively high stability of H^- and Mu^- in many semiconductors and wide-gap oxides, to account for the $\approx$1-μs lifetime of the signal. Both requirements must be fulfilled in order to justify the Mu^- assignment. However, the first point, the high electron mobility, lacks a real foundation and the second, the prompt formation of the hydridelike Mu^- configuration, is unlikely since this stable Mu^- state has a complex structure [6–12], and therefore its formation via $\mu^+ \rightarrow Mu^0 \rightarrow Mu^-$ by two-electron capture requires a considerable lattice rearrangement which is unlikely at low temperatures in a short time. Thus, both assignments, μ^+ and Mu^-, are not well founded.

In our model [1], the fast relaxing signal in Al_2O_3 and other systems [13–16] is assigned to an intermediate configuration (transition state) which is formed epithermally and has paramagnetic characteristics with an almost diamagneticlike frequency behavior. The transition state may be described as a muonium complex with the electron slightly separated from the muon, but weakly bound to it. Such configurations have

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been observed recently in experiments on TiO_2 and $SrTiO_3$ [17–19]. The well-defined hyperfine lines of these states indicate that the muon-electron (polaron) complex is formed promptly (in the nanosecond time range) after implantation. The muon-polaron concept was also applied in Ref. [20].

We suggest that the transition state (seen as a fast relaxing diamagneticlike signal in several experiments) [7,10,13–16,21–23] has the same origin and structure as the above-mentioned states in TiO_2, $SrTiO_3$, and Cr_2O_3, the only difference being that the electron is not localized in an atomic-scale region (small polaron) but is distributed over some area (large polaron) and probably also somewhat more distant from the muon. Such a configuration is predicted by theoretical calculations for zirconia samples [9]. Thus, in our model, the relaxation of the fast signal is not due to delayed electron capture at μ^+ but is a property of the transition state.

For the formation of the transition state, we propose that the muon picks up the electron in the charge-exchange regime and stops as compact muonium in the unrelaxed lattice. Strain release promotes the electron out of the cage to a neighboring site. The necessary energy, if required, comes from the strain release by this transition. An energy problem as conjectured in the Comment does not exist since the electron is not promoted into the vacuum but only from the "constrained" muonium to a conduction-band-like configuration.

The main argument for delayed muonium formation is based on electrical-field measurements. However, these experiments cannot distinguish whether the weakly bound state is formed epithermally as assumed in our model or by delayed capture of an electron from the ionization track. The pulling effect of the electric field is the same, either by avoiding electron capture into the weakly bound state or by detracting the electron from a weakly bound state as assumed in our model. We should mention here that the transition state is not static but corresponds to a dynamical (hot) situation with rapid configuration changes involving situations with weak electron binding. Thus, electric-field sensitivity as such does not distinguish between the two models.

The authors argue that the anisotropy of the electrical-field effect proves that a radiolytic electron from the incoming side of the muon is captured. However, charge effects (even after the periodic reversal of the field), e.g., positive charges along the muon track or at the surface, could provide a pulling field on the electron increasing the force of the applied electric field in this direction. We would also like to mention that in our transition state model the electron of the muon-polaron complex could well be preferentially on the incoming side of the muon. This would, e.g., be the case if the electron is separated from the muon in the last step before stopping. Thus, the anisotropy of the electric-field effect is not an argument against our model.

The authors claim that lattice relaxations, which play a role in our model, are fast and can therefore not be relevant in the present case. However, processes in which energy barriers are involved can be rather slow. In this case, the conversion rate is reduced from the usual attempt rate, which is in the order of the Debye frequency (around 10^{13} s^{-1}), by the factor $\exp[-E_a/(kT)]$ where E_a is the barrier height, k is the Boltzmann constant, and T is the temperature. Thus the conversion rate can become practically zero at low temperatures, leading to a metastable situation. Reaction barriers are expected for transitions between different configurations and are predicted in theoretical calculations [9]. We would also like to mention that in conventional implantation processes, e.g., in the semiconductor industry, annealing procedures are almost always required to obtain the desired configuration.

The thermal spike model, which we applied to muon implantation [14], was developed in the context of heavy-ion research in order to describe the structural changes of the material due to the passage of an ion through matter. In this model, the energy loss of the ion produces a heating of the material in a small cylindrical channel which subsequently induces changes in the bonding structure of the sample [24]. Excellent description of latent track formation for a large variety of experimental conditions (different ions and different materials) is obtained. We have adopted this model to describe reactions of muonium with the host lattice. Here the thermal spike is due to the energy deposited at the end of the muon trajectory, partially due to the stopping process itself, but also due to the stress release when the muonium electron escapes from the strong binding to the muon. The thermal spike effect disappears at higher temperatures since this extra energy diffuses rapidly into the surroundings before the reaction takes place. The thermal spike model provides a plausible and consistent interpretation of the increase of the diamagnetic fraction at low temperatures in μSR experiments [14].

In conclusion, we have pointed out some questionable aspects of the delayed capture model and have answered to the critical comments about our model. Finally, we would like to mention the proof of the paramagnetic nature of the fast relaxing signal: the frequency shift reported in our transition state paper [1], also observed in solar cell absorber materials [15] and in fused quartz [25], indicates that a paramagnetic electron is present during the lifetime of the state and thus contradicts the assumption that the state is diamagnetic and ends by conversion to paramagnetic muonium. The frequency shift occurs only at low magnetic fields (typically smaller than a few millitesla) and has probably been overlooked in other cases.

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