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

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Vilão *et al.* (Phys. Rev. B **96**, 195205 (2017) and Phys. Rev. B **99**, 195206 (2019)) have reported positive muon spin rotation/relaxation (μ^+SR) experiments on various insulating metal oxides, solar cell materials, and alloyed Ge. They note the presence of a separate early component in the μ^+ polarization time dependence which relaxes more rapidly than the longer lived signal and also exhibits (in ZrO_2:Mg) a slightly increased frequency at low temperature in transverse field. They interpret this early component as a weakly bound "transition state" of the neutral muonium (Mu $= \mu^+e^-$) atom formed epithermally by the incoming 4-MeV muon, in which the hyperfine interaction between the muon and the electron is "motionally narrowed" by rapid spin exchange, resulting in a "diamagneticlike" Larmor precession signal. This "diamagneticlike transition state" supposedly takes microseconds to relax into its final ground state due to the reluctance of the surrounding lattice to deform around the Mu atom. However, numerous earlier experiments (including those in electric fields) on various liquids and solids ranging from wide-gap insulators to narrow-gap semiconductors have convincingly shown that Mu formation proceeds through capture of radiolysis electrons by thermalized muons—a process crucially dependent on the electron mobility rather than epithermal dynamics. Therefore, we question the validity of the interpretation by Vilão *et al.* and raise some important issues that need clarification.

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The production of ions and free electrons by ionizing radiation has been implicated in the implantation of 4-MeV "surface muons" in insulators since the earliest days of μ^+SR. At first, the complexities of radiolysis and geminate recombination were largely ignored, in the belief that muonium (μ^+e^- or Mu) atoms always formed in nonmetals and were sometimes rendered diamagnetic through "hot atom" chemical reactions while still epithermal [1]. The spectacular dependence of the probability of muonium formation on the *phase* of neon gives an important clue [2]. The ionization energy of Ne (21.56 eV) exceeds that of Mu (13.539 eV), so the μ^+ cannot "steal" an electron from a Ne atom. As expected, epithermal processes yield almost no Mu in the gas phase and very little in the liquid; and yet 80% of muons manage to capture an electron in solid Ne, because radiolysis electrons from the muon's track are far more mobile in the solid than the liquid. Experiments in liquid helium [3], cryocrystals [4] like solid nitrogen [5,6], and solid and liquid rare gases [7,8] showed conclusively that the μ^+ thermalizes "downstream" of the free electrons liberated in its ionization track and often captures one of those radiolysis electrons to form Mu. This was demonstrated by applying electric fields parallel or antiparallel to the beam direction. The former dramatically reduces Mu formation by pulling the muon and its nearest track electron apart. The latter pushes early track electrons toward the muon so that more electrons are involved in muonium formation and Mu formation in weak electric fields is often enhanced (for details, see Ref. [8]). The more Mu is formed, the smaller is the diamagnetic (or "diamagneticlike") signal; in cryoliquids and cryocrystals, both diamagnetic[like] and Mu precession are observed directly and the fractions add up to 100%. That relatively modest E fields can compete with the Coulomb attraction of the positive muon for electrons implies that they spend time separated by at least dozens of nm. This fact has established the background for developing a technique for measuring electron mobility in solids and liquids on a microscopic scale [5] inaccessible to conventional time-of-flight methods. Application of this technique allowed tracking the evolution of the electron mobility over five orders of magnitude in crystalline nitrogen [5] and detection of fast and slow electrons in liquid Ne [7]. These discoveries imply that both solid N_2 and liquid Ne support delocalized electron

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states (band states) that exhibit electron mobilities comparable to those of conventional semiconductors ($\approx 10^3$ cm^2 V^{-1} s^{-1}). Because of the unique properties of liquid helium, the time of muonium formation varies from 70 ns in superfluid ^{4}He to 10 μs in normal helium, as has been observed directly in the polarization function. In solid neon at 22 K, where the muonium formation is too fast to be observed directly, by varying the transverse magnetic field strength and observing its effect on the initial phase and amplitude of muonium precession we were still able to *measure the timescale* of "delayed" electron capture: about 2.2 ns [8].

Similar results are observed in a wide variety of insulators and semiconductors, including crystalline SiO_2 [9], NaCl, Si [10], GaAs [11–13], GaP [14], and CdS [15]. In sapphire (Al_2O_3) [16], the same effect was observed at room temperature, but at 20 K the effect of electric fields was reversed: a parallel field *reduced* the "diamagneticlike" signal while an antiparallel field *increased* it [17]. The Mu signal itself was very rapidly relaxed in sapphire by (perhaps among other things) ^{27}Al nuclear dipoles. The "diamagneticlike" signal in sapphire at low temperature has a slowly relaxing part attributed to a "bare" μ^+ and a faster relaxing part whose relaxation rate ($\approx 1\ \mu s^{-1}$) is too fast to be attributed to nuclear moments. It is the latter component which is quenched by a parallel electric field, showing clearly that it has something to do with radiolysis electrons. This was tentatively attributed to generation of an anomalously high density of highly mobile radiolysis electrons at low temperature, resulting in preferential formation of the negative ion Mu^-, an outcome regarded by Cox *et al.* [18] as implausible—perhaps justly, although the negative charge state of hydrogen or muonium is known to be quasistable in many semiconductors [19] and wide-gap oxides [20].

In 2017, Vilão *et al.* [21] proposed a model of the muon's end-of-track behavior in which the fast-relaxing diamagneticlike signal in Al_2O_3 and assorted other metal oxides is attributed to a "transition state" of neutral muonium, Mu_T, formed from the initial "hot" muonium atom Mu^{0*} by some unspecified process, which somehow causes the Mu electron to be weakly bound and the hyperfine interaction to be both weak and subject to rapid spin exchange with the lattice, allowing precession at almost the same frequency as the bare μ^+. There are indeed confirmed examples of such "weakly bound states" of Mu in various semiconductors [22], so this much might seem plausible except for the assumption that deeply bound Mu^{0*} somehow spontaneously excites into "shallow" Mu_T without any external source of energy. Furthermore, the ability of strong electric fields to prevent the formation of such weakly bound states of Mu has been demonstrated in GaAs, GaP, and CdS; but such electric field effects are almost *symmetric* with respect to the *direction* of the electric field, contrary to the behavior seen in sapphire. However, the explanation by Vilão *et al.* of why the Mu_T state takes on the order of 1 μs to "relax" into a long-lived Mu^0 state rests on a supposed inability of the lattice to relax quickly in response to its distortion by Mu_T. This is extremely implausible, considering the ubiquity of "lattice polarons" in which free electrons and their accompanying lattice distortions form quasiparticles. Surely the timescale for lattice relaxation is on the order of phonon periods—usually on the order of picoseconds.

It also ignores the *energetics* of the proposed transition: The hypothetical Mu^{0*} precursor is supposed to involve a compact Mu atom, whose electron is perforce bound by a significant fraction of a Rydberg. After the transition, this is supposed to become (among other possibilities) a "shallow" Mu_T state or a bare μ^+, either of which is (at most) barely bound at all. Where did the energy come from for this boost?

Vilão *et al.* recently went on to claim [23] that an increasing diamagnetic signal with decreasing temperature signifies a "thermal spike" at the end of the muon's radiation track, as opposed to a radiolysis "spur" of positive ions and free electrons. This is more than simply renaming the known effects of radiolysis; it completely ignores the role of free electrons in thermal Mu formation.

In Ref. [21], the authors mention only the mysterious case of sapphire [16,17] (where the amplitude and relaxation rate of the fast-relaxing "diamagneticlike" signal increase up to 45 K, above which no diamagnetic signal is observed) and the formation of "weakly-bound" (binding energy on the order of $\approx$10 meV) Mu states (WBS) in high-mobility, low-effective-mass semiconductors like GaAs [11,12,24]. They correctly assert that our model of delayed Mu formation presumes that the weakly bound state is formed by delayed capture of an electron from the ionization track. However, their following statement that justification of this model is largely based on electric field measurements which show that the state is easily ionized, indicating weak binding of the electron, is clearly a misrepresentation. While we may have unadvisedly used the term "ionization" in Ref. [24], we also made it abundantly clear that, in a weak external electric field, the electron "falls to the muon" *through* this WBS. An applied electric field biases the muon-electron potential by adding a linear gradient to the Coulomb attraction. If the resulting linear potential gradient across the electron's orbit produces a bias comparable to the binding energy in the absence of the applied field, the WBS *never forms* (so neither does any deeper state) and the electron escapes. This is explicitly a property of high-mobility, low-effective-mass semiconductors where such WBS are well documented [15,22]. Such a WBS can either be observed directly by measuring its hyperfine coupling or be revealed by electric field experiments. In fact, the employment of electric fields effectively suppresses the unwanted influence of the muon track and can even enable selection of the final muon species to probe the local environment.

Delayed Mu formation in cryocrystals [4–6,8], other solids [9,10], and liquids [7,25,26] may or may not involve a WBS, as abundantly apparent from the diverse electric field dependences observed in those cases, from which we have drawn unambiguous conclusions. Any other interpretation of delayed Mu formation requires a plausible alternative explanation of the electric field effects, based on solid experimental evidence and, in particular, consistent with reasonable expectations of timescale and energetics.

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