Dynamics and Reactivity of Positively Charged Muonium in Heavily Doped Si:B and Comparisons with Hydrogen

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The detailed dynamics of the positively charged muonium (Mu^+) in heavily doped p-type Si:B is reported. Below 200 K, Mu^+ is static and isolated, and is located in a stretched Si-Si bond. Above $\approx$ 200 K, Mu^+ diffuses incoherently. At temperatures higher than 300 K, the Mu^+-B^- complex is formed while above 520 K, it starts to dissociate. There is significant enhancement of the diffusion of Mu^+ in Si compared to H^+ and D^+—this is attributed to its smaller mass.

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The dynamics of light interstitials in solids has received a lot of attention [1–8]. Many of these studies have been focused on understanding the motion and interactions of these interstitials inside their host [1–4]. An example of an important light interstitial is hydrogen (H). It easily enters many materials, such as semiconductors, where it rapidly passivates impurities and defects, resulting in dramatic modifications of the host's electrical and optical properties [3–5]. Although much information has been obtained on the H-impurity complexes in semiconductors [6–8], it is much more difficult to study the *isolated* precursor states of H (i.e., H^+, H^-, and H^0) because of their high diffusivities and reactivities. Moreover, the effect of the interstitial's mass on its dynamics is still not fully understood [9].

Consider the specific case of H^+ in Si. This is one of the unique systems where detailed studies of the dynamics of the singly charged isolated H isotopes are available [10]. However, the observed effects were not different enough to clearly identify the quantum isotopic effects. This could be related to the fact that the mass of the studied isotope (deuterium) is not dramatically different from H. Therefore, it is crucial to study an ultralight H isotope, such as muonium ($Mu = \mu^+ e^-$), since it is expected that the quantum isotopic effects will get greatly enhanced [9]. Recall that the muon has a lifetime of 2.2 μs, spin 1/2, and mass of approximately 1/9 that of the proton [11]. Hence, it can be considered a light pseudoisotope of the proton. This makes Mu^+ in Si a potentially ideal system for testing quantum diffusion theories and investigating the importance of quantum isotopic mass effects.

Because of the muon's short lifetime, it is generally much easier to study the *isolated* states of muonium compared to hydrogen [11–18] using the muon spin relaxation (μSR) technique. However, despite the decades of studies on muonium in many semiconductors, surprisingly little information exists regarding Mu^+ in Si. In particular, although previous muon-decay positron channeling experiments have inferred that Mu^+ resides in the Si-Si bond center (BC) [19], quantitative information on the location of the nearest neighbor Si atoms with respect to the muon does not exist. Moreover, quantum diffusion processes and the reactivity of Mu^+ in Si have not been carefully characterized. Consequently a direct comparison of isotopic effects with H^+ in Si is still missing. These difficulties arise from the fact that such studies are possible only if one is able to study the magnetic and/or electric interactions between the muon and the host nuclei. However, since only a small fraction of the Si host atoms have nonzero magnetic moment, i.e., ^{29}Si, abundance 4.7%, spin 1/2, the muon experiences only weak nuclear dipole interactions (there is no quadrupole interaction for spin 1/2 nuclei).

In this Letter, we report the detailed quantum dynamics of Mu^+ in Si. This is made possible by investigating the time dependence of the muon polarization to long times ($\sim$10 muon lifetimes) in heavily doped p-type Si:B. The isolated Mu^+ is found to be static until about 200 K, above which phonon-assisted incoherent quantum diffusion is observed. At higher temperatures, Mu^+ is trapped at an impurity (boron) and undergoes rapid local tunneling around it. Above $\approx$ 520 K, the complex dissociates. Quantitative information characterizing the structure of the low temperature isolated Mu^+ center, its mobility, and the structure and stability of the muon-impurity complex is reported. We also found significant enhancement in the quantum isotopic mass effects in the dynamics of Mu^+ compared to H^+ and D^+ in Si.

The μSR studies were carried out at the pulsed muon facility ISIS in the United Kingdom. A highly spin-polarized ($\simeq$ 100%) beam of muons with nominal energy of $\simeq$ 29 MeV/c is implanted into the sample, a $\langle 100 \rangle$ p-type heavily doped Si:B single crystal with thickness of 0.63 mm and boron concentration $\sim 10^{18}$ cm^{-3}. The quantity of interest in these experiments is the time dependence of the muon spin polarization $P(t)$ [11]. The large

concentration of holes in the Si:B sample implies that the Fermi level is close to the valence band, and thus the formation of the positively charged state of muonium (Mu^+) is preferred [10,20]. This is confirmed by muon spin rotation studies which show that essentially all the signal is due to a nonparamagnetic state. The measurements reported here were carried out in the absence of an applied field. The pulsed nature of the incoming muon beam at ISIS means very few random background counts are recorded [11], and hence this facility is capable of detecting very slow depolarization rates, a fact that is crucial to the success of our current experiments.

Figure 1 shows typical time-dependent muon polarization spectra at 11 and 290 K. There is a weak relaxation of the signal that is more noticeable at low temperatures. Since these experiments were conducted in the absence of an applied field, this relaxation is due entirely to the dipolar interaction of the muon with the relevant nuclei in the sample, such as ^{29}Si, ^{10}B, and ^{11}B. The relaxation is also clearly temperature dependent, indicating that the local environment of the muon is changing with temperature. In order to parametrize the relaxation, and hence obtain quantitative information on its temperature dependence, the data at all temperatures were modeled with the "static Kubo-Toyabe" (sKT) function [21] $P_s(t) = \frac{1}{3} + \frac{2}{3}(1 - \Delta^2 t^2)e^{-(\Delta^2 t^2/2)}$. The sKT function is strictly valid for a static center precessing in isotropic random Gaussian-distributed magnetic fields, in which case Δ is a measure of the distribution of the local internal fields experienced by the muon. In fact, other models will provide more accurate physical descriptions of $P(t)$ at certain temperatures and they will be used as needed in order to extract accurate fundamental parameters from the data. Nevertheless, $P_s(t)$ gives good fits of the experimental data at all temperatures, and therefore Δ can be used as a convenient phenomenological measure of the muon depolarization rate.

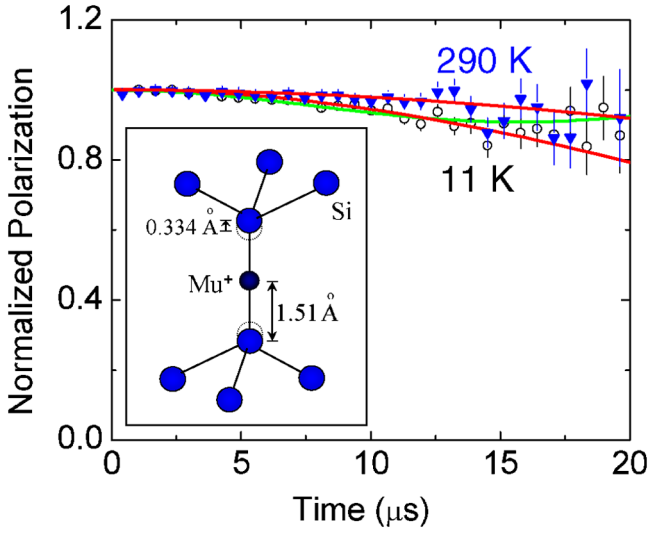

FIG. 1 (color online). Time-dependent muon polarization spectra at 290 K (triangles) and 11 K (circles). The solid red (gray) curves are fits to the static Kubo-Toyabe function, while the solid green (light gray) curve is the fit to the 11 K data as described in the text. The inset is a schematic of the Mu^+ in the Si-Si bond, which is stretched by $\approx 29\%$.

The temperature dependence of Δ is shown in Fig. 2. These values were obtained from fits of the data to $P_s(t)$ starting from 2 μs to avoid early times distortions in the signal due to the pulsed nature of the beam. Note that the value of Δ is much smaller than for Mu^+ in other III-V semiconductors such as GaAs where all the host nuclei have magnetic moments [18]. This is qualitatively consistent with the small natural abundance of ^{29}Si in the sample, which therefore means that there is only a small probability that a Mu^+ is next to a host nucleus with a nonzero magnetic moment. Five distinct temperature regions, labeled I through V in Fig. 2, can be identified. Below, we will elaborate on the structure and dynamics of the Mu^+ in each of these regions and if appropriate, compare with the results of H^+ in Si.

In region I, i.e., below ≈ 200 K, Δ is temperature independent, indicating that the Mu^+ experiences the same dipolar field independent of temperature. In other words the Mu^+ is static (and isolated) in this region. According to muon-decay channeling measurements by Simmler *et al.* [19], Mu^+ in Si resides near the center of the Si-Si bond, i.e., at the BC site. Our $P(t)$ data can be used to estimate the distance r_{Si} between the Mu^+ and its neighboring Si nucleus. This can be accomplished by calculating the time-dependent polarization [11] from the Hamiltonian $\mathcal{H}$ describing the dipolar interaction between the muon and one ^{29}Si neighbor, i.e., $\mathcal{H} = D(I_{x'}K_{x'} + I_{y'}K_{y'} - 2I_{z'}K_{z'})$ where I and K are the Mu^+ and ^{29}Si spin operators, respectively. (The probability that the Mu^+ is near a ^{29}Si

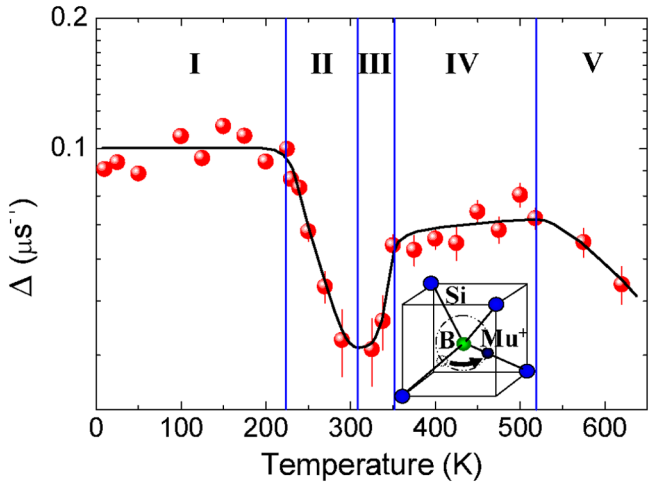

FIG. 2 (color online). Temperature dependence of the muon relaxation rate Δ obtained from fitting the μSR data to the static Kubo-Toyabe function. The inset shows schematically the tunneling of Mu^+ around the B.

nucleus is also taken into account.) The dipolar tensors are assumed to be axially symmetric around the Mu-Si direction z' which is at an angle $\theta = 54.74°$ with respect to z (the muon polarization direction). Fits to the experimental $P(t)$ enable us to estimate the strength of the dipolar interaction $D = \mu_0 h \tilde{\gamma}_\mu \tilde{\gamma}_{\mathrm{Si}}/4\pi r_{\mathrm{Si}}^3$, where μ_0 is the permeability of free space, h is Planck's constant, $\tilde{\gamma}_\mu = 135.5374$ MHz/T and $\tilde{\gamma}_{\mathrm{Si}} = 8.4655$ MHz/T are the gyromagnetic ratios of Mu^+ and ^{29}Si, respectively. The value of the Mu^+-Si distance is found to be $r_{\mathrm{Si}} = 1.51 \pm 0.03$ Å. (Typical fit is the green or light gray curve shown in Fig. 1.) Since the undistorted length of the Si-Si bond is 2.35 Å, this indicates that the Si-Si bond is stretched by $\approx 29\%$ due to the presence of the muon (see inset of Fig. 1) which is somewhat smaller than the $\approx 35\%$ distortion caused by H^+ [10] implying that nuclear masses and zero-point energy play a non-negligible role in lattice distortions.

Above 200 K, i.e., region II in Fig. 2, a decrease in Δ is observed as the temperature is increased. This is a clear signature that Mu^+ is diffusing incoherently through the lattice [9], and the suppression of Δ can be explained as a motional averaging of the local dipolar fields by the mobile Mu^+ [18]. In this region, we are interested in obtaining the hop rate of the isolated Mu^+. This can be done by fitting the $P(t)$ data in this region to the "dynamic Kubo-Toyabe" (dKT) function [21,22] $P_d(t) = P_s(t)e^{-\nu_i t} + \nu_i \int_0^t e^{-\nu_i \tau} P_s(\tau) P_d(t-\tau) d\tau$. Here $P_s(t)$ is the phenomenological expression (given above) describing the polarization of the static Mu^+ (with an average value of $\Delta = 0.097\ \mu s^{-1}$ obtained from region I). The quantity ν_i in $P_d(t)$ should be interpreted as the interaction rate of Mu^+ with a ^{29}Si. By assuming that Mu^+ diffuses by moving from one BC site to a neighboring one, its hop rate ν can be calculated using $\nu = \nu_i/0.0914$ [23]. The temperature dependence of ν is plotted in the inset of Fig. 3 and is well described by an Arrhenius law $\nu = \nu_0 e^{-E_d/k_B T}$. The prefactor ν_0 was found to have a range of $(0.45\text{–}10.9) \times 10^{10}\ s^{-1}$ and the activation energy $E_d = (0.19 \pm 0.05)$ eV. The relatively small activation energy indicates that the diffusion mechanism of Mu^+ in Si is not classical over-barrier hopping and it is in fact undergoing quantum tunneling in the Si structure.

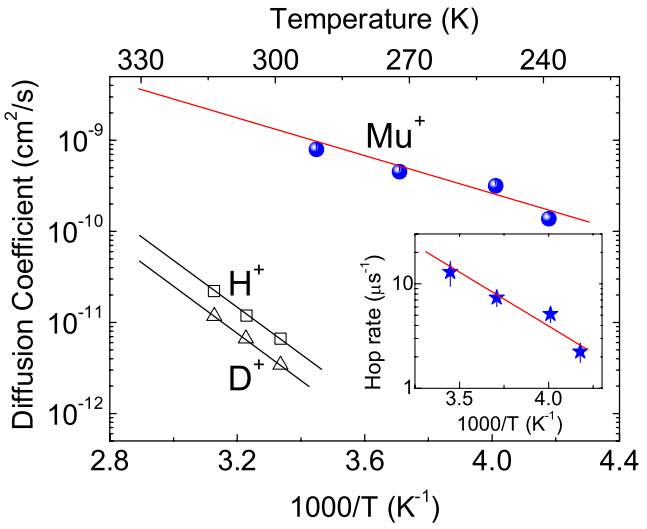

FIG. 3 (color online). Temperature dependence of the diffusion coefficients in Si for Mu^+ compared to H^+ and D^+ obtained by Herring *et al.* [10]. The inset shows the temperature dependence of the Mu^+ hop rate in Si. The solid lines are fits to an Arrhenius law (see text).

Knowledge of the hop rate of isolated Mu^+ enables calculation of its diffusion coefficient $D_d = x^2\nu/6$, where x is the jump length of Mu^+. In the case of Mu^+ jumping between BC sites in the Si lattice, $x = a/\sqrt{8}$ represents the distance between two adjacent BC sites, where $a = 5.43$ Å is the lattice constant of Si. In Fig. 3 we compare the diffusivities of Mu^+ in Si to that of positively charged hydrogen (H^+) and deuterium (D^+) measured using time-resolved capacitance-transients in Schottky diodes under changes of bias [10]. We find the averaged value of the preexponential factor of Mu^+ ($\sim 5.67 \times 10^{10}\ s^{-1}$) is smaller than that of H^+ ($\sim 2.36 \times 10^{13}\ s^{-1}$) [10] by more than 2 orders of magnitude, which is evidence for a strong isotopic mass effect [1,2].

When dealing with tunneling processes, it is important to evaluate the tunneling matrix element J and the coincidence energy E_c [1]. We use the Flynn-Stoneham model [1] in the high temperature limit to fit our data for Mu^+ as well as the data for H^+ and D^+ in Si [10]. We obtain for Mu^+ a tunneling matrix element $J_{\mathrm{Mu}^+} = 1.5$ meV and coincidence energy $E_{c_{\mathrm{Mu}^+}} = 0.2$ eV, whereas we find $J = 56.2$, 56.9 meV and $E_c = 0.51$, 0.52 eV for H^+ and D^+, respectively. These results not only indicate that the transport mechanism of Mu^+ in the Si structure is quantum mechanical, but also reveal an enhanced Mu/H and Mu/D isotopic mass effect over that of H/D. This also suggests that both J and E_c have strong dependence on the nuclear masses [1]. Unfortunately, this dependence is not simple enough to be explained by direct mass scaling.

As the temperature is raised further, i.e., in region III of Fig. 2, Δ increases again. This rise is a signature of *trapping* of the Mu^+ at an impurity [18,22]. Since the most abundant impurity in the silicon host is the intentional dopant boron, we expect it to be the trapping center. This increase in Δ is then due to the presence of nuclear-dipolar fields experienced by Mu^+ while it is part of the Mu^+-B^- complex (see discussion of region IV below). Our goal in region III is to estimate the trapping radius r_t of the B^- nuclei. This can be achieved by using the expression $r_t = \nu_t/4\pi c_t x^2 \nu$ that relates the trapping radius to the trap rate ν_t [24], the isolated Mu^+ hop rate ν, the concentration of boron (traps) $c_t \sim 10^{18}\ cm^{-3}$, and the jump length x defined earlier. An extrapolation of ν in region II to temperatures in region III confirms that the hop rate of isolated Mu^+ is large enough that $P_d(t) \approx 1$. In this limit, the

dynamics governing the trapping process can be solved within a strong-collision approach [11,18,25] to give the polarization function $P_t(t) = e^{-\nu_t t} + \nu_t \int_0^t e^{-\nu_t \tau} P_s(t-\tau) d\tau$ where $P_s(t)$ represents the polarization of the Mu^+-B^- complex. Here, $P_s(t)$ is given by the sKT function given above with $\Delta = 0.065\ \mu s^{-1}$, obtained by averaging the Δs in region IV where we consider the muon to be "fully" trapped. Hence, ν_t can be obtained by fitting the polarization data in region (III) to $P_t(t)$. The subsequent application of the above expression for r_t gives a range of $\approx$ 30–790 Å for the trapping radius [26]. This large trapping radius is appropriate for a Coulomb capture process where the positively charged Mu^+ center is trapping at the negatively charged B^- impurity.

The values of Δ in region IV (see Fig. 2) are essentially constant, indicating that the Mu^+-B^- complex is stable at these temperatures [22]. Interestingly, the values of Δ in this region, and hence the associated effective nuclear-dipolar fields, are much smaller than expected for a *static* Mu^+ located near a boron nucleus. (Recall that 100% of the boron nuclei have magnetic and quadrupole moments.) Consistent with this, estimates of the muon-boron distance assuming a static center interacting via dipolar and muon-induced quadrupolar interactions with the boron yields highly unphysical results. Instead, we suggest that the muon is undergoing rapid local motion (tunneling) between the four equally favored BC sites around a boron nucleus (see inset of Fig. 2), analogous to that seen for the H^+-B^- complex in boron implanted Si [7]. Such motion should average out the boron related dipolar and quadrupolar interactions [27], and if rapid enough, would lead to $\Delta = 0$. The fact that Δ is small but clearly nonzero in region IV prompts us to speculate that the tunneling Mu^+ is still sensing the local fields due to ^{29}Si. By following the procedure outlined for calculating $P(t)$ in region I, the effective muon-silicon distance is estimated to be 1.87 ± 0.13 Å. This value should be compared to that of 1.53 Å for H-Si in the Si-B bond [28]. The muon could be closer to the boron trapping center than H because of quantum effects due to the differences in their masses.

Finally, we briefly address region V of Fig. 2. The higher the temperature, the faster the conversion into the rapidly moving, motionally narrowed, isolated muon state [described by $P(t) = 1$]. This leads to the observed decrease in Δ with increasing temperature.

In summary, we are able to detect the weak nuclear dipole interactions between the Mu^+ and the ^{29}Si host nuclei. This enabled us to investigate the structure of isolated Mu^+, its diffusivity and stability, the resulting lattice distortion, as well as the formation and nature of the Mu^+-B^- complex. We also identified significant enhancement in the dynamics of Mu^+ compared to those of H^+ and D^+ in silicon, which we attribute to quantum effects due to the much smaller mass of the Mu^+.

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