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Muonium dynamics in Si at high temperatures

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We report longitudinal muon-spin-relaxation measurements in intrinsic Si from 350 to 850 K. The data are explained by a two-state model describing alternating charge states of muonium resulting from thermally excited electrons. Within this model, the average muon-electron hyperfine parameter in the neutral state is consistent with muonium at the tetrahedral interstitial site. This indicates that at the highest temperatures measured neutral muonium spends significant time away from the bond center site, the calculated adiabatic potential minimum.

The electronic structure and dynamics of isolated hydrogen in crystalline solids is of fundamental interest since hydrogen is the simplest and also the lightest interstitial impurity. In semiconductors, information on atomic hydrogen has potential technological importance since it passivates the electrical activity of defects and impurities.[1] Due to its high mobility and reactivity, it is difficult to study isolated hydrogen. In fact there has been only one direct observation of isolated hydrogen in a semiconductor by conventional means—the electron spin resonance identification of the $AA9$ center in Si at 77 K as bond-centered hydrogen.[2] In contrast, our understanding of muonium (μ^+e^-—essentially a light hydrogen isotope) in semiconductors is far more advanced because it is easier to produce isolated muonium and study it using muon spin rotation and related techniques.[3]

Muonium (Mu) centers are formed when positive muons are implanted in a wide variety of semiconductors. In Si at low temperatures, three distinct centers can be experimentally distinguished—two neutral paramagnetic centers Mu_T (called *normal muonium*) and Mu_{BC} (called *anomalous muonium* or Mu*) in addition to a charged diamagnetic center (Mu^+ and/or Mu^-). Mu_T has an isotropic muon hyperfine (hf) parameter approximately 45% that of free muonium and appears to be moving rapidly between tetrahedral interstitial (T) sites.[3] This is confirmed by calculations which predict that muonium at or near the T site has a large contact hyperfine parameter and a small adiabatic potential energy barrier between adjacent T sites.[4] At low temperatures, Mu_{BC} is immobile on the time scale of the muon lifetime (2.2 μs) and is characterized by a small anisotropic muon hf interaction with the majority of the electron spin density located on the two neighboring Si atoms which are on the $\langle 111 \rangle$ axis of symmetry.[5] The observed inversion symmetry along with the values of the muon and ^{29}Si hyperfine parameters are proof that this center is Mu_{BC}, a neutral muonium atom located at the center of an expanded Si-Si bond.[5] Theory[4] predicts that the global minimum in the adiabatic potential energy of the neutral muonium or hydrogen is at or very near the bond-center (BC) site, if the surrounding lattice atoms are allowed to relax fully. This is supported by a study of electron-irradiated Si at 15 K which shows that Mu_T converts to Mu_{BC}.[6] However, at high temperatures adiabaticity is expected to break down. For example, molecular-dynamics calculations of an interstitial proton in Si ($T > 1200$ K) show that the surrounding host atoms do not have time to respond to the fast motion of the proton.[7] Such nonadiabatic motion should occur at lower temperatures for muonium since the muon has only $\frac{1}{9}$ the proton mass.

Previous muon-spin-relaxation (μSR) experiments[3,8] below room temperature have shown that both Mu_T and Mu_{BC} ionize with activation energies of a few tenths of an eV implying levels near a band edge, although it is not clear whether the final state is Mu^- or Mu^+. Decay pos-

itron channeling results[9] at room temperature imply that the ionized species resides near the BC site, leading to the common assignment of Mu^+ for the ionized species based on theoretical arguments that Mu^- is unstable at the BC position.[4] Above 400 K the muon $1/T_2$ relaxation rate rises rapidly indicating that the inverse reaction also takes place ($Mu^{\pm} \rightarrow Mu$).[11]

In this paper we report extensive measurements of the longitudinal muon spin $1/T_1$ relaxation in nominally pure Si as a function of magnetic field (0.015–6 T) and temperature (350–850 K). The relaxation is described by a two-state model in which a single muonium state undergoes repeated cycles of ionization followed by capture of an electron from the conduction band. Relaxation results from hyperfine oscillations in the neutral charge state. From a global fit of $1/T_1$ we obtain an average isotropic hyperfine parameter A_μ of muonium while in the neutral charge state, an energy level in the gap and an average cross section for electron capture. The fitted A_μ is closer to that predicted for Mu_T rather than Mu_{BC} suggesting that neutral muonium spends a significant amount of time at or near the T site, as would result if the motion of the muonium were nonadiabatic.

In our model for the muon spin relaxation, with assumptions as discussed below, the muon is in thermal equilibrium with thermally generated conduction electrons and has an energy level E_μ in the upper part of the band gap (E_g). Assuming thermal equilibrium the probability p_0 that the muonium with twofold spin degeneracy ($g=2$) is neutral may be written as

$$p_0 = \frac{\lambda_{+0}}{\lambda_{0+}+\lambda_{+0}} = \frac{1}{1+(1/g)\exp[(E_\mu - E_F)/k_B T]} \quad (1)$$

leading to

$$\lambda_{0+} = \tfrac{1}{2}\lambda_{+0}\exp[(E_\mu - E_F)/k_B T] , \quad (2)$$

where λ_{+0} and λ_{0+} are the rates for electron capture and ionization, respectively, and E_F is the Fermi level. If a magnetic field is applied along the initial muon spin polarization, then after each charge exchange cycle a small field-dependent amount of polarization will be lost on average due to the muonium hyperfine oscillation and the fact that the captured electron is unpolarized. The spin dynamics of muonium undergoing charge exchange, first considered by Ivanter and Smilga,[10] can be solved for arbitrary λ_{0+} and λ_{+0} using various approaches.[11–13] A useful approximate expression for $1/T_1$ is

$$1/T_1 \approx \frac{\lambda_{0+}\lambda_{+0}}{\lambda_{0+}+\lambda_{+0}} \left[\frac{2\pi^2 A_\mu^2}{\lambda_{0+}^2 + 4\pi^2 A_\mu^2 + 4\pi^2 B^2 (\tilde{\gamma}_e + \tilde{\gamma}_\mu)^2} \right] , \quad (3)$$

where B is the magnitude of the applied magnetic field $\mathbf{B}$ and $\tilde{\gamma}_e$ and $\tilde{\gamma}_\mu$ are the gyromagnetic ratios (in MHz/T) of the electron and muon, respectively.

The experiments were performed at the M15 beamline at TRIUMF which provides a beam of nearly 100% spin-polarized positive muons. Conventional time-differential μSR measurements of $1/T_1$ were made, with the magnetic field applied along the initial muon spin direction, on a high-purity float-zoned Si crystal obtained from TOPSIL which had a nominal resistivity of 33 000 Ω cm at room temperature with a net acceptor concentration of $\approx 5\times 10^{11}$ cm^{-3}. As shown in Fig. 1, excellent fits to the μSR time spectra were obtained by assuming that the muon spin polarization $G_{zz}(t)$ has the form $\exp[-t/T_1]$. Figure 2 shows the fitted values of $1/T_1$ at four of the six temperatures where detailed field scans were carried out. The curves are a fit to the above model for $1/T_1$ spin relaxation with the capture rate taken as $\lambda_{+0}=\sigma v n$, where σ is an average cross section for an electron in the conduction band to be captured by Mu^+, n is the electron concentration in the conduction band, and v is the average thermal velocity of the electron. The ionization rate λ_{0+} is then given by Eq. (2). Three parameters (σ, E_μ, and A_μ) were used to fit the data; σ and $E_\mu - E_F$ were assumed to be temperature independent with E_F located at midgap while A_μ was allowed to vary with temperature. (The fitted parameters change slightly if we assume E_μ/E_g is constant and the temperature dependence of E_g is as given by Ref. 14.)

Several assumptions made in the analysis should be discussed. (1) Thermal equilibrium is established by the present measurements which demonstrate the occurrence of rapid charge cycling. (2) Although the majority of data was obtained with **B** oriented parallel to a ⟨110⟩ crystallographic direction, several measurements were also made with **B** along a ⟨100⟩ direction. If the muon-electron hf interaction of the neutral muonium were highly anisotropic, $1/T_1$ would be orientation dependent. Such a dependence was not observed. Furthermore, as indicated by Fig. 2, $1/T_1$ at low fields is relatively flat whereas at high fields, it is proportional to B^{-2}. This is characteristic of an isotopic hf interaction [see Eq. (3)] whereas a highly anisotropic hf interaction normally leads to quite different behavior. Hence, the hf interaction is best described as being isotropic as assumed in our model. (3) Figure 3(a) shows the temperature dependence

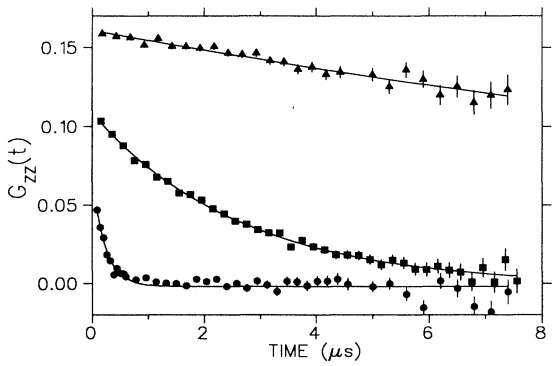

FIG. 1. The muon spin polarization $G_{zz}(t)$ in nominally pure Si at 500 K for 0.1 T (circles), 0.5 T (squares), and 1.5 T (triangles). The curves are fits to a single exponential relaxation function.

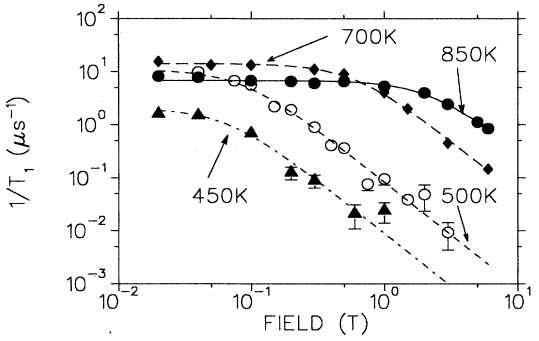

FIG. 2. The muon $1/T_1$ relaxation rate in nominally pure Si as a function of magnetic field. The curves are the best global fit to the charge-exchange model described in the text.

of $1/T_1$ in pure Si. Above 600 K the lifetime of neutral Mu is less than the period of a hyperfine oscillation so that the amount of polarization lost per cycle diminishes and consequently $1/T_1$ falls off ("motional narrowing"). The downturn of the curve shown in Fig. 3(a) is obtained from the model providing further confirmation that $1/T_1$ is due to rapid cycling of the charge state of muonium. (4) The assumption that E_μ is in the upper part of the band gap is confirmed by relaxation measurements in doped samples which show enhanced relaxation for the n-type and reduced rates for the p-type material, indicating that the charge-exchange process involves a positive ionized state and conduction electrons.[15] (5) Since a general temperature dependence of the capture cross section is not available in the literature, the assumption of a temperature-independent σ was made in the analysis. If σ is assumed to be proportional to T^N, with $N \neq 0$, the fitted values of A_μ below 600 K can differ significantly from those plotted in Fig. 3(b).[16] However, they do not vary significantly above 600 K and hence do not affect the primary conclusions.

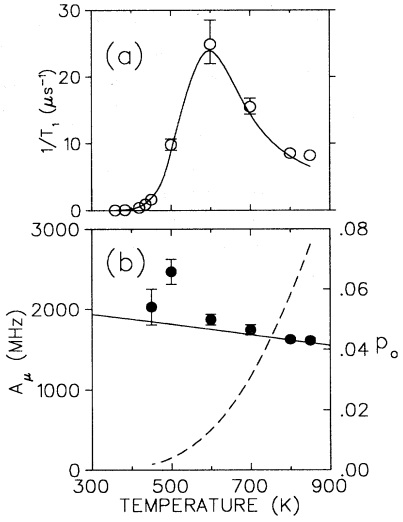

FIG. 3. (a) $1/T_1$ in nominally pure Si (circles) in low fields. The magnetic field was 15 mT for $T < 450$ K and between 20 and 40 mT for $T \geq 450$ K. These data closely approximate the temperature dependence for constant low field since at these low fields $1/T_1$ is only weakly field dependent. The curve indicates the best-fit results to the model. (b) The average muon-electron hyperfine parameter A_μ and the fraction of time in the neutral state p_0 in nominally pure Si. The points are the fitted hf parameters obtained. The solid line is an extrapolation of μSR results for the hf parameter of Mu_T below 300 K. The dashed line indicates the temperature dependence of p_0 from Eq. (1).

Figure 3(b) shows the fitted values for A_μ and the fraction of time the muonium is in the neutral state [i.e., p_0 determined via Eq. (1)] as a function of temperature. The error bars in A_μ are primarily systematic originating from the uncertainty in the literature values for n.[17,18] The solid curve is an extrapolation of direct μSR measurements of A_μ for Mu_T from below 300 K.[19] The agreement is remarkable considering that the present data were obtained indirectly by fitting high-temperature measurements of $1/T_1$ to a dynamical charge-exchange model. The fitted values for A_μ are more than an order of magnitude larger than the isotropic hf parameter of Mu_{BC}. The fact that A_μ is similar to Mu_T is consistent with nonadiabatic muonium motion. The muonium spends a significant fraction of its time near the T site since a much smaller lattice relaxation is required there than for Mu occupying the BC site. Nonadiabatic behavior has been invoked previously to explain the existence of metastable Mu_T at low temperatures in Si,[4] the disagreement between the theoretical and experimentally determined isotropic hf parameter of normal muonium in GaAs,[20] and the local tunneling motion of the Mu^I center in CuCl.[21] The actual dynamics are more complicated than suggested by our two-state model since a diffusing muon samples many locations with different hf parameters. However, the lack of orientation dependence, the qualitative behavior of $1/T_1$ in low and high magnetic fields (discussed above), as well as the appreciable relaxation in high fields indicate that the muon is experiencing a large isotropic hf interaction for a significant fraction of its lifetime [p_0 in Fig. 3(b)]. This is difficult to explain if adiabaticity is valid since in such a framework the total energy of a muon/muonium at a BC site is usually calculated to be at least ≈ 0.3 eV below that at a T site,[4,22] implying that the BC site should be occupied much more frequently.

Two other parameters which govern the charge-exchange dynamics of muonium, and presumably hydrogen, were obtained from the fit to the two-state model. The thermal average cross section for an electron in the conduction band to be captured by Mu^+ is $\sigma = 2.8(3) \times 10^{-15}$ cm^2 and the Mu 0/+ level is 0.34(1) eV below the conduction-band edge, with purely statistical errors shown. This is larger than the Arrhenius activation energy characterizing the disappearance of Mu_T and the appearance of Mu^+ below 300 K where the ionization process is suggested to involve the intermediate state Mu_{BC}.[8] If this more complicated model involving

two sites were valid at high temperatures, a $T \leftrightarrow$BC site change may be intimately tied to electron ionization and capture.[22] In this case, the fitted energy of 0.34 eV could be interpreted as an activation energy for the reaction $Mu_T^0 \rightarrow Mu_{BC}^+ + e^-$ involving both ionization and a site change and would not be directly associated with the $0/+$ level for either site.

In conclusion, we have performed extensive measurements of muon spin $1/T_1$ relaxation in intrinsic Si at high temperatures and find them consistent with rapid charge cycling between the neutral and positive charge state of muonium. We find that the neutral state is similar to normal Mu at the T site, as indicated by the magnitude of its average hyperfine interaction.

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