Diffusion and Charge Dynamics of Negatively Charged Muonium in *n*-Type GaAs

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(Received 31 October 1995)

We report measurements on the dynamics of negatively charged muonium (Mu^-) from 295 to 1000 K in heavily doped *n*-type GaAs:Si. The Mu^- center begins to diffuse above 500 K with a hop rate described by an Arrhenius function $\nu = \nu_0 e^{-E_\mu/k_B T}$ where $\nu_0 = 5.6(5) \times 10^{12}\ \mathrm{s}^{-1}$ and $E_\mu = 0.73(1)$ eV. Above 700 K, relaxation from charge-state fluctuations is observed. The analysis of these data implies $\mathrm{Mu}^- \leftrightarrow \mathrm{Mu}^0$ conversions occur via alternating capture of holes and electrons, establishing Mu as a deep recombination center. Similar dynamics are expected for the isolated H^- center in *n*-type GaAs. [S0031-9007(96)00189-5]

PACS numbers: 71.55.Eq, 66.30.Jt, 76.75.+i

Considerable work [1] has been devoted to obtaining microscopic descriptions of hydrogen centers in elemental and compound semiconductors. Any of the three charge states of isolated interstitial hydrogen (H^0, H^+, H^-) may contribute to the diffusivity and hence reactivity of H in semiconductors. However, experimental information on the physical and electronic structure of these centers is available only for neutral atomic H, and only for Si, while information on the *dynamics* of all three centers is virtually nonexistent. Consider the H^- center in *n*-type GaAs. Although its existence has been inferred from reverse-bias annealing experiments [2], alternative explanations for these data have been proposed [3]. Furthermore, the diffusion profile of H is complicated [4], leading to speculation that more than one charge state is involved, in particular, H^0 and H^-. Therefore any additional source of information on either the diffusion or charge states of H in GaAs would enhance our understanding of these impurities.

Muonium ($\mathrm{Mu} = \mu^+ e^-$) is well established as an experimental model for H in semiconductors. The positive muon (μ^+, spin 1/2) has a mass m_μ approximately 1/9th that of the proton m_p and therefore Mu behaves like a light isotope of H. In this paper we report detailed measurements of the diffusion and charge-state dynamics associated with the negatively charged muonium center (Mu^-) in metallic *n*-type GaAs:Si. Our results demonstrate that the diffusion rate of Mu^- is orders of magnitude slower than for the neutral tetrahedral interstitial Mu_T^0 in semi-insulating GaAs. At the highest temperatures investigated, these data provide the first demonstration of Mu as an electron-hole recombination center and yield the most detailed information to date on the nature of one of the Mu charge cycles which have been observed in many semiconductors. Although direct comparisons of Mu and H dynamics are complicated by the large mass ratio and resulting quantum effects, these results provide a semiquantitative model of the dynamics of isolated H in *n*-type GaAs.

The techniques used to study Mu require only a small number of muons (typically one) in the sample at a time; hence, Mu-Mu interactions are nonexistent. Furthermore, because of their short average lifetime (2.2 μs), they are studied within a few microseconds after implantation. This allows experiments on *isolated* Mu to be carried out with relative ease. In the past such experiments have provided detailed information on the local electronic structure of the *neutral* (paramagnetic) muonium centers [5]. The (diamagnetic) Mu^- center in heavily doped *n*-type GaAs [6] was characterized only recently and quantitative information regarding the diffusion of Mu^+ and Mu^- is currently unavailable. Experiments at high temperatures show that the charge on Mu cycles is due to repeated ionization and recapture of electrons or holes [7,8]. Such processes can be probed much more directly for Mu than for H and should be the same for the two species since they depend only weakly on the mass of the nucleus. In contrast, as stated above, comparison of the diffusion rates is more complicated.

The majority of the experiments were performed at TRIUMF and some at ISIS. Positive muons with $\approx$100% spin polarization were implanted into the sample, a wafer of Bridgman-grown *n*-type GaAs:Si (from Laser Diode, Inc.) with a net donor concentration of $4.5 \times 10^{18}\ \mathrm{cm}^{-3}$ and a (110) face. In muon spin rotation (μSR) experiments [9] the observed quantity is the time evolution of the muon spin polarization. In the transverse-field (TF) geometry the initial muon spin is perpendicular to the applied magnetic field **B** and undergoes Larmor precession about the sum of this field and any internal fields. In the longitudinal-field (LF) geometry, **B** is directed along the initial polarization direction while in zero field (ZF) $B = 0$.

 0031-9007/96/76(20)/3790(4)$10.00 © 1996 The American Physical Society

The muon polarization in a TF-μSR experiment can be written as $P_{\rm TF}(t) = G_{\rm TF}(t)\cos(\omega_\mu t)$ where $\omega_\mu = \gamma_\mu B$ is the Larmor frequency with a muon gyromagnetic ratio of $\gamma_\mu = 2\pi \times 135.54\ \mu{\rm s}^{-1}\,{\rm T}^{-1}$. Information about the dynamic processes is obtained from the relaxation function $G_{\rm TF}(t)$. If the $\rm Mu^-$ center is static, the surrounding nuclear spins give rise to a spread in the internal fields which is well described by a Gaussian relaxation function; i.e., $G_{\rm TF}(t) \propto \exp(-\sigma^2 t^2)$ where σ is a measure of the distribution of nuclear magnetic dipolar fields at the muon sites [9]. If the muon is hopping at a rate $\nu = 1/\tau_c$ which is fast compared with σ, the linewidth is reduced since the dipolar interaction is motionally averaged. Furthermore, $G_{\rm TF}(t)$ deviates from Gaussian, approaching an exponential if ν is large [9]. A second source of spin dynamics may occur if Mu is undergoing charge-state changes as a result of interactions with free carriers. Such reactions are either unidirectional or cyclic and also result in an exponential decay of the precession.

It is difficult to distinguish between fast hopping and charge-state changes solely from the functional form of $G_{\rm TF}(t)$ since both processes give rise to exponential relaxation functions. ZF and LF measurements can, however, distinguish between the two types of dynamics, as well as provide better quantitative estimates of dynamical parameters. If the muon is stationary, its polarization in zero field is described by the static Kubo-Toyabe function [10]: $p(t) = \frac{1}{3} + \frac{2}{3}(1 - \Delta^2 t^2)\exp[-\frac{1}{2}\Delta^2 t^2]$. The parameter $\Delta = \gamma_\mu \langle B_\mu^2 \rangle^{1/2}$ characterizes the distribution of the local fields. If the muon is diffusing, the muon polarization is given by the "dynamic Kubo-Toyabe" (DKT) function [10]: $P_{\rm ZF}(t) = p(t)e^{-\nu t} + \nu \int_0^t p(\tau)e^{-\nu\tau}P_{\rm ZF}(t-\tau)\,d\tau$ which can be solved numerically for $P_{\rm ZF}(t)$. In a system such as GaAs where the internal fields at the muon are due to nuclear dipoles, a magnetic field of magnitude $B \approx 0.01$ T is sufficient to "quench" or suppress the relaxation for diamagnetic Mu, i.e., to give $P_{\rm LF}(t) = 1$. In contrast, if Mu is undergoing cyclic charge changes, significantly larger fields are needed. Suppose that the charge changing reaction involves the neutral center $\rm Mu^0$ with an *isotropic* hyperfine (hf) interaction and one charged (diamagnetic) center, in our case $\rm Mu^-$. The relaxation is described [7] by $G_{\rm LF}(t) = e^{-t/T_1}$, with

$$\frac{1}{T_1} = \left(\frac{\lambda_{0-}\lambda_{-0}}{\lambda_{0-} + \lambda_{-0}}\right)\frac{2\pi^2 A_\mu^2}{\lambda_{0-}^2 + \omega_{24}^2}, \qquad (1)$$

where λ_{-0} and λ_{0-} are the rates of conversion for $\rm Mu^- \rightarrow Mu^0$ and $\rm Mu^0 \rightarrow Mu^-$, respectively. The field-dependent frequency $\omega_{24} = 2\pi A_\mu(1 + x^2)^{1/2}$ where A_μ is the isotropic hf parameter of $\rm Mu^0$ in frequency units, $x = B(\gamma_e + \gamma_\mu)/2\pi A_\mu$, and $\gamma_e = 2\pi \times 27992.48\ \mu{\rm s}^{-1}\ {\rm T}^{-1}$ is the gyromagnetic ratio of the electron.

Figure 1(a) shows a typical TF-μSR spectrum from $\rm Mu^-$ in our heavily doped n-type GaAs sample. The damping of the precession is Gaussian near room temperature, characterized by the linewidth parameter σ. The temperature dependence of σ is plotted in Fig. 1(b). Although the relaxation approaches an exponential at the highest temperatures, only the *qualitative* dependence of σ is needed in our investigation. Previous experiments at room temperature have established that the diamagnetic center in GaAs:Si samples of similar dopant concentration is isolated $\rm Mu^-$ located near a $T_{\rm Ga}$ site [6] (tetrahedral interstitial with Ga nearest neighbors). We label this center as $\rm Mu_T^-$. The Gaussian form of the relaxation establishes that the muon is not undergoing long range diffusion during periods of a few muon lifetimes. As illustrated in Fig. 1(b), the temperature independent σ indicates that $\rm Mu_T^-$ remains static until $\approx$500 K (region I). Above this temperature, $\rm Mu_T^-$ begins to diffuse, as evidenced by the decrease in σ (region II). Application of a small longitudinal magnetic field of $\approx$0.01 T is sufficient to fully quench the relaxation, indicating that it is due to weak nuclear dipolar fields. The increase in σ beginning at $\approx$700 K (region III) is attributed to cyclic charge exchange involving a neutral center $\rm Mu^0$. An irreversible transition such as $\rm Mu_T^- \rightarrow Mu^0$ is not consistent with the LF-μSR data discussed below.

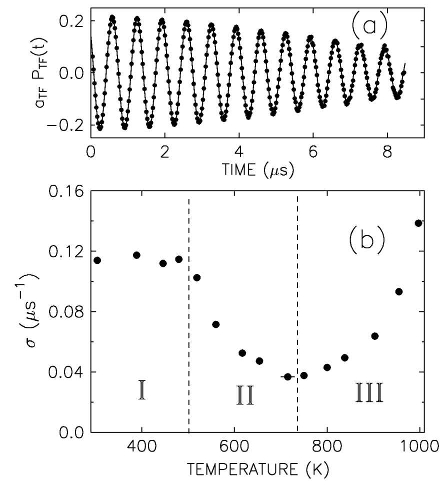

FIG. 1. (a) An example of a TF-μSR spectrum, measured at $\approx$295 K with B$\|\langle 110\rangle$ axis in n-type GaAs:Si. The solid line is the best fit to the data. (b) The temperature dependence of the Gaussian linewidth parameter σ. The three regions are described in more detail in the text.

More precise estimates of the muon hop rate ν in region II were obtained from ZF-μSR measurements. Typical data are shown in Fig. 2(a). First, the static Kubo-Toyabe function is used to fit the ZF data below $\approx$400 K where the muon is static, giving $\Delta = 0.165(5)\ \mu{\rm s}^{-1}$. The value of Δ is then fixed and the data from 475 to 625 K are fitted by the DKT equation to obtain ν. The temperature dependence of ν is plotted in Fig. 2(b). A fit by an Arrhenius law $\nu(T) = \nu_0 e^{-E_\mu/k_B T}$ yields $\nu_0 = 5.6(5) \times 10^{12}\ {\rm s}^{-1}$ and an activation energy $E_\mu = 0.73(1)$ eV. In a simple model where the muon makes random jumps in three dimensions between the nearest *equivalent* tetrahedral interstitial sites in the zinc-blende lattice [5], the diffu-

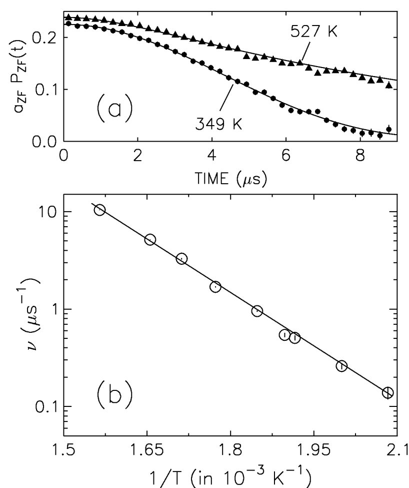

FIG. 2. (a) Examples of ZF-μSR spectra for *n*-type GaAs:Si. The solid lines are best fits to the data. (b) The temperature dependence of the hop rate ν. The solid line is the best fit assuming an Arrhenius functional form.

sion constant is $D_\mu = a^2\nu/12$, where a is the lattice constant (=5.64 Å in GaAs). Thus we obtain $D_\mu = 1.5(1) \times 10^{-3} \exp[-0.73(1)\ \mathrm{eV}/k_BT]\ \mathrm{cm}^2/\mathrm{s}$. As a comparison, Chevallier *et al.* [4] report a diffusion constant for deuterium in heavily doped *n*-type GaAs of $4 \times 10^{-12}\ \mathrm{cm}^2/\mathrm{s}$ at 513 K while $D_\mu(513\ \mathrm{K}) = 1.1 \times 10^{-10}\ \mathrm{cm}^2/\mathrm{s}$. The ratio of these diffusion constants is considerably larger than predicted by classical mass scaling arguments assuming the same processes, suggesting that quantum or nonadiabatic effects are important as might be expected with such light particles. However, the differences may also be a consequence of the different time scales of the two types of experiments. The bulk diffusion constant of deuterium may be limited by trapping and detrapping at dopant atoms whereas on the short time scale of the Mu_T^- measurements, such interactions are unimportant.

The hop rate for the neutral Mu_T^0 center in GaAs [11] at room temperature is roughly 9 orders of magnitude faster than reported here for Mu_T^-. The reduced diffusivity of Mu_T^- is consistent with theoretical calculations [12]. The minimum energy configuration for both states is expected near the T_{Ga} site. However, although both the T_{Ga} and T_{As} sites are comparable in energy for Mu^0, the ionicity of GaAs lowers the energy for Mu^- in the T_{Ga} region due to Coulomb interactions and raises the energy of the T_{As} region. Consequently, the energy barrier for Mu_T^- to hop to the next equivalent site is larger than for Mu_T^0. In addition, a significant lattice distortion around Mu_T^- as suggested by previous data [6] would reduce the tunneling matrix element.

The LF data above 700 K (region III) are well described by $P(t) = e^{-t/T_1}$. Large fields are required to quench the relaxation [see Fig. 3(a)] verifying that the depolarization is due to cyclic charge changes [13]. Two paramagnetic centers, labeled as $\mathrm{Mu}_{\mathrm{BC}}^0$ and Mu_T^0, are known to exist in GaAs. The former is immobile at the bond center [14] and has a small highly anisotropic hf interaction while the latter is a highly mobile state characterized by an *isotropic* hf interaction $A_\mu = 2884$ MHz at low temperatures [15]. Our measurements of the field dependence of $1/T_1$ at 900 and 1000 K clearly show that the neutral center has a large and isotropic hf interaction. Hence, we assume that only Mu_T^- and Mu_T^0 are involved in the charge dynamics, i.e., $\mathrm{Mu}_T^- \rightarrow \mathrm{Mu}_T^0$. This also represents the simplest and most plausible cycle since both states should be located near a T_{Ga} site.

At each temperature, the transition rate λ_{0-} for conversion from Mu_T^0 to Mu_T^- and the rate λ_{-0} for the reverse can be determined from the measured $1/T_1$ rates at two fields using Eq. (1). Since the hf parameter is assumed to be close to that of Mu_T^0, it is not necessary to invoke detailed balance or to assume a functional form for the temperature dependence of the rates, as was done in Ref. [7]. The experimental $1/T_1$ rates at $B \approx 48$ mT and $B \approx 2.9$ T are shown in Fig. 3(a) and the λ_{-0} and λ_{0-} rates obtained from these data are displayed in Figs. 3(b) and 3(c), respectively. The dashed line through the data for λ_{-0} [Fig. 3(b)] represents a fit by $\lambda_{-0} = \lambda_0 e^{-E_{-0}/k_BT}$ and gives $\ln(\lambda_0/\mu\mathrm{s}^{-1}) = 25.1(1.5)$ and $E_{-0} = 1.66(7)$ eV. E_{-0} is close to the value of the gap in GaAs, providing strong evidence that a band gap excitation governs this process. In contrast, the rate λ_{0-} [Fig. 3(c)] is only weakly dependent on temperature,

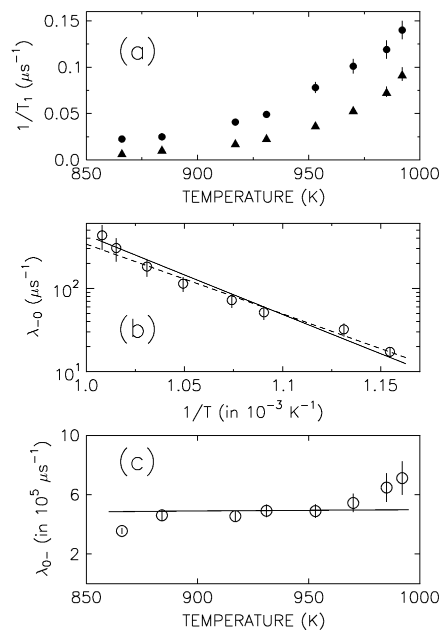

FIG. 3. (a) The temperature dependence of the $1/T_1$ rates at $B = 2.9$ T (triangles) and $B = 48$ mT (circles). (b) The temperature dependences of the rate for $\mathrm{Mu}^- \rightarrow \mathrm{Mu}^0$. The dashed line is the best fit to the data assuming an Arrhenius function while the solid line is the best fit assuming that $\mathrm{Mu}^- + h^+ \rightarrow \mathrm{Mu}^0$. (c) The rate for $\mathrm{Mu}^0 \rightarrow \mathrm{Mu}^-$ and the corresponding fit.

implying that the conversion from Mu_T^0 to Mu_T^- is not an activated process.

The cyclic reaction $\mathrm{Mu}_T^- \rightarrow \mathrm{Mu}_T^0$ can occur via interaction with either electrons or holes. As discussed below, the most consistent explanation of the data is that charge conversions occur via alternating capture of holes from the valence band and electrons from the conduction band, i.e., $\mathrm{Mu}_T^- + h^+ \rightarrow \mathrm{Mu}_T^0$ and $\mathrm{Mu}_T^0 + e^- \rightarrow \mathrm{Mu}_T^-$. The rates are then given by $\lambda_{-0} = \sigma_h p v_h$ and $\lambda_{0-} = \sigma_e n v_e$ where p and n are the h^+ and e^- concentrations, respectively, v_h and v_e are their thermal velocities [16], and σ_h and σ_e are the cross sections for h^+ and e^- capture (i.e., the free parameters in our analysis). Since the material is very heavily doped, n is essentially constant in this temperature region and has the extrinsic [16] value (4.5×10^{18} cm^{-3}). The h^+ concentration is $p \approx n_i^2/n$ where n_i is the intrinsic carrier concentration [16,17]; hence $p \propto \exp[(-1.52\ \mathrm{eV})/k_B T]$. The functional forms of v_h and v_e are given in Ref. [16] and have weak $T^{1/2}$ dependences. Hence, provided that σ_h and σ_e do not vary drastically in this temperature region, the functional forms of λ_{0-} and λ_{-0} assuming alternate electron and hole trapping are fully consistent with our experimental data. As noted above, λ_{-0} is Arrhenius-like with an activation energy similar to the band gap while λ_{0-} is essentially temperature independent. The best fits, shown as the solid lines in Figs. 3(b) and 3(c), give average cross sections of $\sigma_h = 2.6(2) \times 10^3$ Å^2 and $\sigma_e = 16.0(6)$ Å^2 [18]. The remaining possibilities (1) $\mathrm{Mu}_T^0 \rightarrow \mathrm{Mu}_T^- + h^+$ and (2) $\mathrm{Mu}_T^- \rightarrow \mathrm{Mu}_T^0 + e^-$ are unlikely. Both are activated processes and should produce an Arrhenius temperature dependence for λ_{0-} and λ_{-0}. The weak temperature dependence of λ_{0-} [Fig. 3(c)] rules out process (1). On the other hand, process (2) is more difficult to discard because λ_{-0} is actually well described by an Arrhenius function [Fig. 3(c)]. However, as indicated previously, the corresponding fit gives a pre-exponential factor of $\lambda_0 \sim 10^{17}$ s^{-1} which is too large by several orders of magnitude to be physically reasonable.

The alternate trapping of e^- and h^+ makes Mu a recombination center, a common behavior for deep level defects. Note also that the cross section for hole capture is $\approx$2600 Å^2 and that for electron trapping is $\approx$16 Å^2, both reasonable when Coulomb attraction is present or absent, respectively. Finally, we point out that although Mu spends much more time as the charged species at high temperatures (i.e., $1/\lambda_{0-} \ll 1/\lambda_{-0}$), extrapolation of the experimental mobility data on Mu_T^0 below room temperature [11] implies that the diffusion is likely to be dominated by the neutral species. Since charge-state fluctuations should not depend significantly on m_μ and m_p, similar dynamics should also occur for H. Although a quantitative statement about H diffusion rates based on Mu is not possible, one is led to the distinct possibility that the diffusion of H in n-type GaAs at high temperatures is controlled by the transient H^0 species present during charge cycling.

In conclusion, the dynamics of the Mu_T^- center were investigated from 295 to 1000 K. Mu_T^- begins to diffuse above $\approx$500 K with a hop rate well described by an Arrhenius function. Cyclic charge-state changes occur above $\approx$700 K and are modeled assuming $\mathrm{Mu}_T^- \rightarrow \mathrm{Mu}_T^0$. The results imply that the conversion from Mu^0 to Mu^- occurs via electron capture whereas the process $\mathrm{Mu}_T^- \rightarrow \mathrm{Mu}_T^0$ involves hole capture, demonstrating that Mu_T is a recombination center in GaAs.

This work is partially supported by NSERC of Canada (K. H. C., R. F. K., S. R. D.), the Robert A. Welch Foundation [Grants No. C–1048 (T. L. E.) and No. D–1053 (R. L. L.)], and the U.S. National Science Foundation [Grant No. DMR–9220521 (T. L. E. and B. H.)]. K. H. C. would also like to thank Dr. W. Hayes for his support.

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