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# Identification of neutral bond-centered muonium in $n$-type semiconductors by longitudinal muon-spin relaxation

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We report measurements of the longitudinal field-dependent muon-spin relaxation rate ($T_1^{-1}$) in $n$-type Si and GaAs under conditions where coherent spin precession of muonium is unobservable. A peak in $T_1^{-1}$ as a function of magnetic field is observed and shown to be characteristic of neutral bond-centered muonium ($\mathrm{Mu}_{\mathrm{BC}}^0$) experiencing spin-exchange scattering with free carriers. These results establish that neutral $\mathrm{Mu}_{\mathrm{BC}}^0$ does not convert to negatively charged muonium in $n$-type Si below approximately 200 K and is present in metallic $n$-type GaAs:Si at 5.5 K.

Two neutral paramagnetic muonium ($\mathrm{Mu}=\mu^+e^-$) centers are formed when positive muons are implanted at low temperature into a wide variety of semiconductors such as Si, Ge, diamond, GaP, and GaAs.[1] These centers have been labeled *normal muonium* ($\mathrm{Mu}_T^0$) and *anomalous muonium* ($\mathrm{Mu}_{\mathrm{BC}}^0$ or Mu*) and are qualitatively similar from one semiconductor to another. $\mathrm{Mu}_T^0$ has an isotropic muon-electron hyperfine (hf) parameter $A_\mu$ of $\approx 2000$ to 3500 MHz depending on the semiconductor, and diffuses rapidly between tetrahedral ($T$) interstitial sites.[2] $\mathrm{Mu}_{\mathrm{BC}}^0$ is immobile on the time scale of the muon lifetime and is located close to a bond-center (BC) position.[3] The hf interaction of $\mathrm{Mu}_{\mathrm{BC}}^0$ is axially symmetric about a $\langle 111\rangle$ crystalline axis and is described by two parameters $A_{\|}$ and $A_{\perp}$ which are approximately an order of magnitude smaller than $A_\mu$. In $n$-type semiconductors above the donor ionization temperature, there are a significant number of free electrons with which Mu can interact. In this situation, two types of interactions involving the neutral centers are expected to dominate: (1) electron capture to form $\mathrm{Mu}^-$ and (2) repeated rapid electron spin-exchange scattering where the spins of the Mu and conduction electrons "flip-flop." For Si, supercell-based adiabatic calculations predict that $\mathrm{Mu}^-$ at the $T$ site is the overall ground state in $n$-type materials and that $\mathrm{Mu}^-$ at the BC site is very high in energy.[4] Therefore, $\mathrm{Mu}^-$ at the BC site is expected to be unstable. A similar situation regarding the charged centers is also expected to occur in GaAs.[5] Consequently, in the case of Mu at the BC site the cross section for electron capture to form $\mathrm{Mu}^-$ is likely to be much smaller than for electron spin exchange since the former would involve a simultaneous change in muon site. On the other hand, for Mu at the $T$ site $\mathrm{Mu}^-$ can be formed without a change in muon site and thus the cross section for electron capture should be much larger. In highly doped $n$-type Si the muon spin precession signals from the Mu signals are rapidly damped above the temperature where there is significant donor ionization, confirming the strong interaction with electrons in the conduction band.[1,6] Although the precession signals are difficult to ob-

 

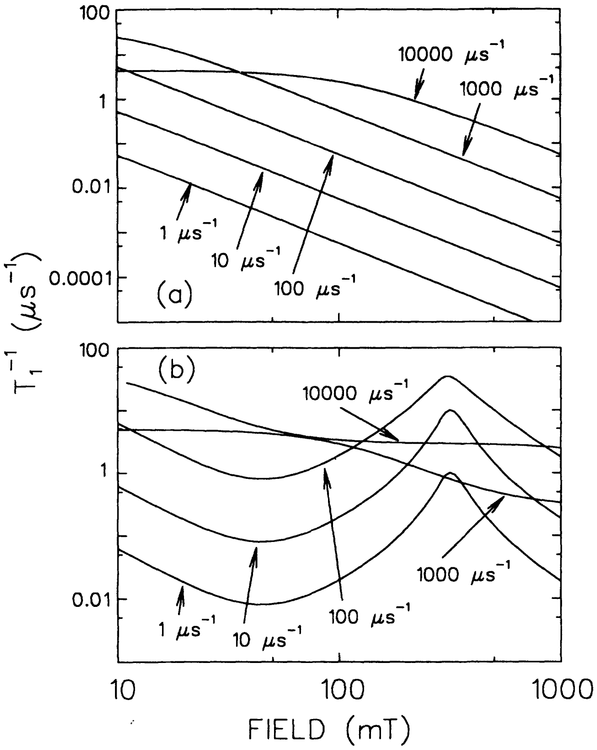


FIG. 1. Theoretical simulations of the field dependence of $T_1^{-1}$ for $\mathrm{Mu}_{\mathrm{BC}}^0$ in Si as a function of various $\nu_{\mathrm{SE}}$ with (a) $\theta=0°$ which is equivalent to isotropic Mu with $A_\mu=A_\perp$ and (b) with $\theta=70.53°$.

serve under these circumstances, measurements of the muon spin polarization in a longitudinal magnetic field can be used to identify any long-lived paramagnetic species and determine the relevant cross sections.

In this paper we report measurements of the longitudinal field (LF) muon spin $T_1^{-1}$ relaxation in $n$-type Si and GaAs which we attribute to $\mathrm{Mu}_{\mathrm{BC}}^0$ undergoing rapid spin exchange with conduction electrons. We show that the field dependence of the relaxation rate provides a distinctive signature of the nature of the muonium center. These results clearly establish the presence of long-lived $\mathrm{Mu}_{\mathrm{BC}}^0$ in heavily doped $n$-type semiconductors at temperatures where significant donor ionization has occurred.

The phenomenological model used to describe the spin dynamics of Mu undergoing spin-exchange scattering was developed by Nosov and Yakovleva.[7] Loss of electron polarization is described by introduction of a phenomenological spin-exchange rate $\nu_{\mathrm{SE}}$ to the equations of motion for the electron and mixed polarization components. Figure 1(a) shows a simulation of the field dependence of the muon $T_1^{-1}$ as a function of the Nosov-Yakovleva spin-exchange rate $\nu_{\mathrm{SE}}$ specifically for the case of $\mathrm{Mu}_{\mathrm{BC}}^0$ in Si ($A_{\|}=-16.82$ MHz, $A_\perp=-92.59$ MHz) for the choice of $\theta=0°$, where $\theta$ is the angle between the *applied* magnetic field $\mathbf{H}_0$ and the $\mathrm{Mu}_{\mathrm{BC}}^0$ hf symmetry axis. Since the LF muon polarization for $\mathrm{Mu}_{\mathrm{BC}}^0$ with $\theta=0°$ is exactly equivalent to that for isotropic Mu with $A_\mu=A_\perp$, this case is equivalent to spin exchange of *isotropic* Mu. The depolarization of the muon spin is well described by a single relaxing component of the form $\exp(-t/T_1)$. In agreement with other recent calculations on isotropic Mu,[8,9] regardless of the spin-exchange rate $\nu_{\mathrm{SE}}$, $T_1^{-1}$ is relatively flat at low fields, decreases as the field is increased, and approaches an $H_0^{-2}$ dependence at high fields where $\nu_{\mathrm{SE}}$ is less than the field-dependent hf frequency.[10] Figure 1(b) shows the field dependence of $T_1^{-1}$ for $\theta\approx 70.53°$. Note that in the slow spin-exchange limit, a resonantlike feature in $T_1^{-1}$ occurs which reaches a maximum value of $T_1^{-1}\approx\nu_{\mathrm{SE}}$.[11] A similar peak is observed for any $\theta$ away from 0° and 90°, with the peak field depending on $\theta$ as demonstrated below. As one reaches the fast spin-exchange regime, the peak disappears although there are still significant differences in the detailed field dependences compared with the isotropic or $\theta=0°$ case.

The origin and characteristics of the peak in $T_1^{-1}$, as illustrated in Fig. 1(b), are easy to understand qualitatively. Isolated stable Mu in an applied magnetic field $\mathbf{H}_0$ (magnitude $H_0$) can be described by an approximate effective spin Hamiltonian which is valid for high fields and depends on the *electron* magnetic quantum number $M_S$. Here, "high fields" imply that the electron Zeeman interaction greatly exceeds the hf interactions. For each value of $M_S$, the approximate Hamiltonian gives rise to an effective field at the muon which has the following components parallel and perpendicular to $\mathbf{H}_0$:[1,12]

$$H_{\|}=H_0\mp H_p, \quad \text{and} \quad H_\perp=\mp\frac{(A_\perp-A_{\|})\sin 2\theta}{4\tilde{\gamma}_\mu} \quad \text{for } M_S=\pm 1/2, \tag{1}$$

where

$$H_p=\frac{(A_\perp\sin^2\theta+A_{\|}\cos^2\theta)}{2\tilde{\gamma}_\mu}. \tag{2}$$

and $\tilde{\gamma}_\mu$ (=135.54 MHz/T) is the muon gyromagnetic ratio. The total muon polarization is the average over the precession of the muon spins about these effective fields. In general, the muon precesses in a cone of fixed angle about each effective field. Hence, the projection of its polarization onto an axis parallel to $\mathbf{H}_0$ consists of a constant and an oscillating component. As shown in Eq. (1), when $H_0 = H_p$, the muon polarization for states with $M_S=+1/2$ precesses about an effective field which is perpendicular to $\mathbf{H}_0$ (and the initial muon polarization) since $H_{\|}=0$. At this field, the amplitude of the oscillating component is the largest. When $H_0$ is far from $H_p$, this amplitude rapidly goes to zero. A useful approximate picture of LF depolarization is that for small $\nu_{\mathrm{SE}}$, the amount of muon polarization lost per the electron spin-exchange cycle is proportional to the amplitude of these oscillations. Hence, in the slow spin-exchange limit, $T_1^{-1}$ (1) scales linearly with $\nu_{\mathrm{SE}}$ and (2) is expected to reach a maximum near $H_p$. For $\mathrm{Mu}_{\mathrm{BC}}^0$ in Si, $H_p$ = 0.32 T when $\theta$= 70.53°, as shown in Fig. 1(b). Such resonantlike spin relaxation provides a distinctive signature which can be used to determine hf parameters and spin-exchange rates under conditions where Mu spin-precession signals are difficult, if not impossible, to observe.

Conventional time-differential LF-$\mu$SR measurements of $T_1^{-1}$ where the initial muon spin is parallel to $\mathbf{H}_0$ were made at the M13 and M15 beamlines at TRIUMF in the following

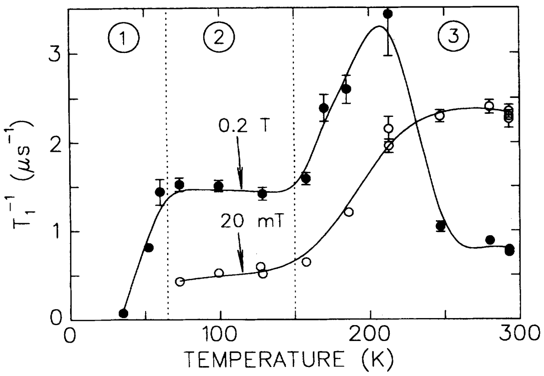


FIG. 2. Temperature dependence of muon $T_1^{-1}$ relaxation rates in $\approx 10^{14}$ cm$^{-3}$ Si:P for $H = 0.2$ T (closed circles) and 20 mT (open circles). The solid curves through the points serve as guides to the eye. The three regions are discussed in the text.

samples: (1) an $n$-type float-zone Si:P sample from General Diode Corporation with a net carrier concentration $\approx 5\times 10^{14}$ cm$^{-3}$ due primarily to phosphorous as measured by photoluminescence (resistivity measurements estimate a net room temperature carrier concentration $\approx 10^{14}$ cm$^{-3}$); and (2) $n$-type metallic GaAs:Si from Sumitomo Electric Industries Ltd. grown by the horizontal Bridgman method with a room temperature carrier concentration of $9\times 10^{16}$ cm$^{-3}$.

In the $\approx 10^{14}$ cm$^{-3}$ Si:P sample $\mathbf{H}_0$ was parallel to one of the four possible $\langle 111\rangle$ crystalline axes so that there are two possible angles $\theta = 70.53°$ and $\theta = 0°$ between the $\mathrm{Mu}_{\mathrm{BC}}^0$ symmetry axis and the applied magnetic field which occur in a 3 to 1 ratio. (The $n$-type Si samples of similar concentration have been briefly studied at low fields by other workers via LF-$\mu$SR and their results are summarized in Ref. 1.) At temperatures greater than $\approx$45 K, the LF muon spin polarization is well described by an exponentially decaying $[\propto \exp(-t/T_1)]$ and a nonrelaxing component. The constant component is attributed to a charged diamagnetic species; most likely $\mathrm{Mu}_T^-$. The temperature dependences of $T_1^{-1}$ for $H = 200$ mT and $H = 20$ mT are shown in Fig. 2. In region 1, $T_1^{-1}$ increases rapidly with temperature and is correlated with ionization of the donors. In region 2, $T_1^{-1}$ is essentially temperature independent while in region 3 there is a sharp initial increase of $T_1^{-1}$ for both fields at $\approx$150 K followed by a crossover occurring at $\approx$230 K. One should note that the relaxation at 20 mT is *smaller* than at 200 mT for $T < 230$ K. Field scans of $T_1^{-1}$ at select temperatures in regions 1 and 2 are shown in Fig. 3(a). Note that a peak in $T_1^{-1}$ occurs at $\approx$0.32 T as predicted for $\mathrm{Mu}_{\mathrm{BC}}^0$. The displayed quantitative fits, using the theoretical approach described above with $\theta = 70.53°$ fixed and $\nu_{\mathrm{SE}}$ as the only adjustable parameter, are in good agreement with the data.[13] If one assumes that $\nu_{\mathrm{SE}} = \sigma n_e v_e$ where $\sigma$ is the cross section for spin-exchange scattering, $n_e$ is the free electron concentration,[14] and $v_e$ is the average thermal velocity of the electron,[15] the fitted values of $\nu_{\mathrm{SE}}$ correspond to an average $\sigma = 4.4(5)\times 10^{-15}$ cm$^2$. The unmistakable identification of $\mathrm{Mu}_{\mathrm{BC}}^0$ leads to the following interpretation of the results in Fig. 2 in the three regions: The rapid increase of $T_1^{-1}$ in region 1 tracks an increasing $n_e$ (and hence $\nu_{\mathrm{SE}}$) due to ionization of the phosphorus donors. In region 2, $n_e$ remains essentially constant, typical of extrinsic behavior; thus, $\nu_{\mathrm{SE}}$ and $T_1^{-1}$ are relatively flat.[16] In the first part of region 3, it is clear that $\mathrm{Mu}_{\mathrm{BC}}^0$ still exists since $T_1^{-1}$ at the higher field is larger than the relaxation rates at the lower field. Previous work has shown that there is significant ionization of $\mathrm{Mu}_{\mathrm{BC}}^0$ in *lightly doped* Si starting at $\approx$130 K.[1] There is sufficient extrinsic electron density in our sample that a $\mathrm{Mu}^+$ ion can quickly retrap an electron; hence, the cyclic charge-exchange process $\mathrm{Mu}_{\mathrm{BC}}^0 \leftrightarrow \mathrm{Mu}^+ + e^-$ also becomes active.[8] Our calculations using the theoretical approach described in Ref. 17 confirm that charge and spin exchange are qualitatively similar—in particular, there is a peak in the field dependence of $T_1^{-1}$ for slow ionization rates which disappears when the ionization is fast. The onset of a second process, i.e., charge exchange, would explain the initial sharp increase of $T_1^{-1}$ in region 3. A possible explanation for the data above 200 K is that the fast charge-exchange regime is eventually reached where $T_1^{-1}$ no longer increases with field, hence the crossover at 230 K. However, recent radio-frequency $\mu$SR studies imply that the dynamics above 200 K are more complicated and involves a BC→$T$ site change.[18] The existence of three distinct temperature regions such as in Fig. 2 is evident in all Si:P samples we have studied with doping levels ranging from $\approx 2\times 10^{13}$ cm$^{-3}$ to $\approx 10^{16}$ cm$^{-3}$. However, for the higher concentrations, a $T_1^{-1}$ peak is not observed above the dopant ionization temperature since the large $n_e$ values lead

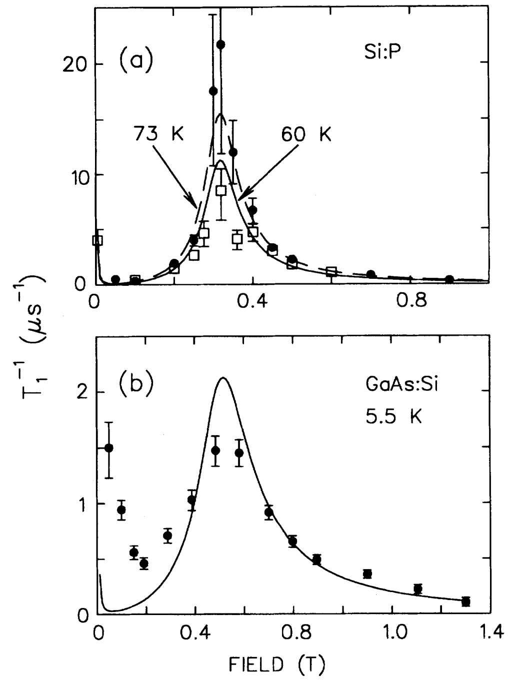


FIG. 3. (a) Field dependence of $T_1^{-1}$ at 60 K (open squares) and 73 K (closed circles) in $\approx 10^{14}$ cm$^{-3}$ Si:P. The solid [$\nu_{\mathrm{SE}}$= 11.2(5) $\mu$s$^{-1}$] and dashed [$\nu_{\mathrm{SE}}$= 15.4(5) $\mu$s$^{-1}$] curves are best fits to the data using the Nosov-Yakovleva theory for 60 K and 73 K, respectively, and assuming $T_1^{-1}$ is due to $\mathrm{Mu}_{\mathrm{BC}}^0$ in Si with $\theta = 70.53°$. (b) The field dependence of $T_1^{-1}$ in metallic $n$-type GaAs:Si at 5.5 K. The line [$\nu_{\mathrm{SE}}$=2.09(6) $\mu$s$^{-1}$] is a best fit to the data assuming the $T_1^{-1}$ is due to $\mathrm{Mu}_{\mathrm{BC}}^0$ in GaAs with $\theta = 54.7°$.

to fast spin exchange. Our results show that in Si:P, $Mu^0_{BC}$ is resistant to forming a negative ion for temperatures below $\approx 200$ K although it undergoes repeated interactions with free conduction electrons. Such behavior implies that there is a substantial energy barrier for the electron capture/site change reaction $Mu^0_{BC}+e^- \rightarrow Mu^-_T$.

The metallic $n$-type GaAs:Si sample was studied with $\mathbf{H}_0$ parallel to a ⟨100⟩ crystalline axis where all orientations between $\mathbf{H}_0$ and the $Mu^0_{BC}$ hf symmetry axis are equivalent with $\theta=54.74°$. Figure 3(b) shows the field dependence of $T_1^{-1}$ at 5.5 K and the corresponding best fit to the Nosov-Yakovleva theory. The poor agreement between the theory and the data at low fields is attributed to the fact that we have not taken into account the nuclear hf interaction of $Mu^0_{BC}$ with the Ga and As host atoms. Nevertheless, the existence of a peak in $T_1^{-1}$ near the expected $H_p$ for $Mu^0_{BC}$ in GaAs ($A_{\parallel}=218.54$ MHz, $A_{\perp}=87.87$ MHz; thus, $H_p=0.48$ T) demonstrates that $Mu^0_{BC}$ is present in metallic $n$-type GaAs and is responsible for a large part of the $T_1^{-1}$ relaxation. This situation should be contrasted to that in *high resistivity* GaAs where at these temperatures the observed $T_1^{-1}$ relaxation is due to $Mu^0_T$ undergoing quantum diffusion.[2] In the metallic sample, $Mu^0_T$ rapidly captures an electron to form $Mu^-$.[19] As in the Si:P samples, the stability of $Mu^0_{BC}$ (to forming $Mu^-$) implies a significant energy barrier for the reaction $Mu^0_{BC}+e^- \rightarrow Mu^-_T$. Furthermore, it is interesting to note that the relatively small value of $\nu_{SE}$ in the metallic GaAs:Si sample argues that only the ionized electrons, i.e., those in the conduction band rather than the impurity bands, contribute to the spin-exchange process. With this assumption, the fitted $\nu_{SE}$ corresponds to $\sigma v_e(5.5\ \mathrm{K})=1.3(1)\times10^{-7}\ \mathrm{s^{-1}\,cm^3}$ and $\sigma=2.3(1)\times10^{-14}\ \mathrm{cm}^2$,[20] roughly comparable to Si:P.

In conclusion, we have observed longitudinal-field muon spin relaxation in $n$-type Si and GaAs. The field dependence of the relaxation provides a clear signature of the $Mu^0_{BC}$ center undergoing slow spin-exchange scattering with conduction electrons. These results significantly expand the temperature and concentration regions for which $Mu^0_{BC}$ has been shown to exist in $n$-type Si and firmly establish its presence in metallic $n$-type GaAs:Si, implying that in these semiconductors the cross section for electron capture by $Mu^0_{BC}$ to form $Mu^-$ is significantly smaller than that for spin-exchange scattering.

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[10] This treatment ignores effects due to fluctuations in the muon hf parameter which could also lead to peaked behavior in $T_1^{-1}$, for example, in R.F. Kiefl *et al.*, Phys. Rev. Lett. **68**, 1347 (1992).

[11] Note that our simulations show two relaxing components for $\theta\neq0°$ and slow spin-exchange rates as established previously for this formalism (Ref. 1). The $T_1^{-1}$ rate constants in Fig. 1(b) are obtained from a least squares fit to the theoretical polarization assuming a single relaxing component $[\propto\exp(-t/T_1)]$ using the same typical binning and time range (i.e., $\approx8\ \mu s$) as the experimental data. Figure 1(b) closely mimics the field dependence of $T_1^{-1}$ for the component with larger amplitude.

[12] C.P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, New York, 1990), p. 521.

[13] The observed $T_1^{-1}$ is due mainly to the $\theta=70.53°$ centers since the contribution from the $\theta=0°$ center is about two orders of magnitude smaller around the peak region ($\approx150-600$ mT), see Fig. 1.

[14] $n_e$ is calculated by assuming that the net impurity concentration is due entirely to phosphorous doped at a level of $5.0\times10^{14}$ $\mathrm{cm^{-3}}$.

[15] M.A. Green, J. Appl. Phys. **67**, 2945 (1990).

[16] Since $v_e \propto \sqrt{T}$ and the effective mass of the electron does not change significantly over this temperature range, $\nu_{SE}$ should change by $\approx50\%$. The flatness of $\nu_{SE}$ hence suggests that $\sigma$ is inversely dependent on velocity.

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[20] $n_e$ is calculated by assuming that the net impurity concentration is due entirely to Si doped at a level of $9.0\times10^{16}\ \mathrm{cm^{-3}}$. In calculating $v_e$, we have assumed that the effective mass $m^*=0.067$ times the mass of the electron.