Novel Behavior of Bond-Centered Muonium in Heavily Doped *n*-Type Silicon: Curie-Like Spin Susceptibility and Charge Screening

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Bond-centered muonium (Mu_{BC}^0) has been observed in very heavily doped *n*-type Si:P. It exhibits a Curie-like electronic spin susceptibility which leads to a giant negative shift in the muon spin precession frequency. At high dopant levels, the Mu_{BC}^0 hyperfine parameters, deduced from a model involving spin exchange with free carriers, are significantly reduced from those in intrinsic Si. This indicates that the spin density distribution for Mu_{BC}^0 in metallic Si:P is altered significantly by charge screening effects, likely a general phenomenon for deep impurities in materials with high carrier concentrations.

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It is well understood how the dopant type and concentration can influence the charge state of impurities in semiconductors. However, very little information exists regarding the effect of the carrier concentration on their electronic structures. Muonium ($Mu^0 = \mu^+ e^-$), a defect which exists as an isolated, amphoteric, deep level impurity in semiconductors, is an ideal candidate for studies aimed at increasing our knowledge of this topic of fundamental interest. Detailed information on muonium in all of its charge states can be obtained using muon spin rotation, relaxation, and/or resonance, i.e., μSR and muon level crossing resonance. As a matter of fact, such studies are the main source of experimental information [1,2] (albeit indirect) on *isolated* hydrogen, an important defect which strongly influences a semiconductor's electrical and optical properties [3].

More is known about muonium in silicon than in any other semiconductor. Previous experiments show that two isolated paramagnetic centers Mu_T^0 and Mu_{BC}^0 coexist after muon implantation. Mu_T^0 diffuses rapidly between tetrahedral (T) interstitial sites and has a large isotropic hyperfine (hf) interaction. On the other hand, Mu_{BC}^0 is immobile on the time scale of the muon lifetime (2.2 μs) and is located close to a bond-center (BC) position with the majority of the spin density on the two neighboring Si atoms. It is characterized by a small, highly anisotropic muon hyperfine interaction which is axially symmetric about a $\langle 111 \rangle$ axis. As predicted by theory, a large diamagnetic signal is also seen which is consistent with Mu_{BC}^+ in *p*-type Si and Mu_T^- in *n*-type materials.

Experiments in lightly doped samples show there is a strong interaction between muonium and free carriers which causes rapid damping of the coherent muonium precession signals in a transverse magnetic field and spin relaxation in a longitudinal magnetic field (see, e.g., Ref. [2]). Two basic types of processes [1,4,5] have been identified: (1) charge exchange whereby the muonium center captures or loses an electron, and (2) spin exchange whereby an electron in the conduction band scatters quasielastically off muonium. In very heavily doped samples, near or beyond the metal insulator transition, much less is known. In heavily doped *n*-type Si one would expect a rapid conversion of any neutral Mu_T^0 to Mu_T^-, the latter being the predicted stable configuration when the Fermi level is close to the conduction band [6]. The fate of Mu_{BC}^0 is not so clear. In lightly doped *n*-type Si it appears to be metastable, indicating there is an energy barrier between the BC and T sites. It is not obvious whether Mu^0 can remain at the BC site and retain its paramagnetic nature at high doping concentrations. For example, one might expect substantial screening of the positive *charge* of the muon. Even if the charge state remains neutral, a *spin* screening cloud could form at low temperatures as for a Kondo impurity in metals.

In this paper, we report the detection and characterization of neutral bond-centered muonium (Mu_{BC}^0) in heavily doped *n*-type Si in the vicinity of the metal insulator transition. Rapid spin exchange between the free carriers and the bound electron on the muon effectively averages the hyperfine fields on the muon, thereby eliminating the characteristic frequency pattern used to identify muonium in nearly intrinsic semiconductors or insulators. However, the paramagnetic nature of Mu_{BC}^0 is revealed by applying a large external magnetic field which leads to a giant shift in the Larmor precession frequency of the muon. This establishes that Mu_{BC}^0 is metastable even in heavily doped *n*-type Si. Our most important finding is that at the highest carrier concentrations, the hyperfine parameters for Mu_{BC}^0 are reduced significantly compared to those observed previously in intrinsic Si. These results demonstrate for the first time how a high concentration of carriers can significantly alter the spin density distribution (i.e., electronic structure) of a deep level impurity such as muonium in a semiconductor.

The experiments were performed on the M15 and M20B muon beam lines (nominal momentum of 28 MeV/c and spin polarization close to 100%) at TRIUMF where positive muons are implanted into the samples. The standard method of transverse-field muon spin rotation (TFμSR) [1] was used to measure the muon spin precession in a large external magnetic field applied perpendicular to the initial muon spin. Information on the local electronic environment is derived from the spectrum of muon spin precession frequencies. Four samples of Si:P were studied: (1) Si:P-1: 3×10^{17} cm^{-3} ($\rho = 0.038\Omega \cdot$ cm); (2) Si:P-2: 9×10^{18} cm^{-3}; (3) Si:P-3: 16×10^{18} cm^{-3}; and (4) Si:P-4, 1×10^{18} cm^{-3} ($\rho = 0.022\ \Omega \cdot$ cm). These concentrations span the metal-insulator transition occurring at $\approx 3.5 \times 10^{18}$ cm^{-3}. The field was applied parallel to a crystallographic $\langle 100 \rangle$ direction of the Si:P-1, Si:P-2, and Si:P-3 samples, and along $\langle 110 \rangle$ in the Si:P-4 sample.

In the presence of such high carrier concentrations, one does not expect to observe the distinctive pattern of precession frequencies which is typically used to characterize muonium in intrinsic or lightly doped semiconductors. If neutral paramagnetic muonium is present, rapid spin exchange between the conduction electrons and the unpaired electron bound to the muon will average the hyperfine interaction leading to a single precession frequency close to the Larmor frequency of a free muon. Therefore, in zero or weak applied magnetic fields, Mu^0 is then indistinguishable from diamagnetic states of the muon such as Mu^- or Mu^+. However, the paramagnetic muonium center should have a large Curie-like magnetic suspectibility which in high magnetic fields will produce a giant frequency shift relative to the Larmor frequency of the bare muon. Below, we develop a model to quantify this effect.

First, consider free isolated muonium in an applied magnetic field $\mathbf{H}_0$. The spin precession frequencies at high fields where the electron Zeeman interaction greatly exceeds the hf interactions can be derived from an appropriate effective spin Hamiltonian. There are two such frequencies, one corresponding to the electron quantum number $m_s = +1/2$ and the other to $m_s = -1/2$. For each value of m_s, the muon can be visualized as precessing about an effective field $\mathbf{H}_{\rm eff} = (H_{\|}, H_{\perp})$. The components parallel ($H_{\|}$) and perpendicular ($H_{\perp}$) to $\mathbf{H}_0$ are given to an excellent approximation by [1,7]:

$$H_{\|}\left(m_s = \pm\frac{1}{2}\right) = H_0 \mp Z; \quad H_{\perp}\left(m_s = \pm\frac{1}{2}\right) = \mp X\,, \tag{1}$$

where

$$Z = \frac{(A_{\perp}\sin^2\theta + A_{\|}\cos^2\theta)}{2\tilde{\gamma}_{\mu}}; \quad X = \frac{(A_{\perp} - A_{\|})\sin 2\theta}{4\tilde{\gamma}_{\mu}}\,.$$

The angle θ is between $\mathbf{H}_0$ and the symmetry axis of the hyperfine interaction (also the bond axis in the case of $Mu^0_{\rm BC}$), $\tilde{\gamma}_{\mu} = 135.54$ MHz/T is the gyromagnetic ratio of the muon, and $A_{\|}$ and $A_{\perp}$ are the parallel and perpendicular hyperfine parameters, respectively. The two frequencies, given by $\tilde{\gamma}_{\mu}H_{\rm eff}$, are those typically observed in high TF-μSR experiments in lightly doped semiconductors [8]. Now, suppose we are in the extreme spin exchange limit. Thus, the bound electron is "flipping" very rapidly between its $m_s = +1/2$ and $m_s = -1/2$ states. The muon will now precess about a *single* average field $\tilde{\gamma}_{\mu}H_{\rm av}$. Clearly, $\mathbf{H}_{\rm av}$ is just the sum of the two effective fields in Eq. (1) weighted by the population in each of the m_s states:

$$\begin{aligned}\mathbf{H}_{\rm av} &= f_{+1/2}\mathbf{H}_{\rm eff}\left(m_s = +\frac{1}{2}\right) + f_{-1/2}\mathbf{H}_{\rm eff}\left(m_s = -\frac{1}{2}\right)\\ &= (H_0 + \Delta P Z, \Delta P X)\,,\end{aligned} \tag{2}$$

where f_{m_s} denotes the fractional populations in the relevant m_s state. The electron spin polarization is given by $\Delta P = f_{-1/2} - f_{+1/2} \geq 0$. As stated above, if the muonium electron is not polarized, i.e., $\Delta P = 0$, then $\mathbf{H}_{\rm av} = (H_0, 0)$, implying that paramagnetic muonium in the fast spin exchange limit cannot be distinguished from the diamagnetic center. However, if $\Delta P \neq 0$ for some reason, $\mathbf{H}_{\rm av}$ will *not* be equal to $\mathbf{H}_0$ and hence the signature for muonium will be a precession signal at a frequency which is shifted from the Larmor frequency of the bare muon ($\nu_o = \tilde{\gamma}_{\mu}H_0$). One can then express $\mathcal{K}$, a normalized frequency shift, as

$$\begin{aligned}\mathcal{K} &\equiv \frac{\nu_o - \nu_{\rm av}}{\nu_o}\\ &= 1 - \left(1 + \Delta P\,\frac{2Z}{H_0} + \Delta P^2\,\frac{X^2 + Z^2}{H_0^2}\right)^{1/2}\\ &\approx -\Delta P\,\frac{Z}{H_0}\,,\end{aligned} \tag{3}$$

where the last term is valid for $\Delta P \ll 1$. Finally, we can also derive an expression for the temperature dependence of ΔP assuming the electronic magnetic moment of muonium is not screened significantly by the spins of the conduction electrons. This will be true provided the temperature is above the Kondo temperature ($T > T_K$), below which a spin screening cloud is expected to form (see Ref. [9] for a recent discussion). Under such conditions, the $m_s = +1/2$ and $m_s = -1/2$ electronic energy levels are separated by the electron Zeeman energy $\tilde{\gamma}_e H_0$, and the Boltzmann population of these levels is assumed:

$$\Delta P = \frac{1 - e^{-h\tilde{\gamma}_e H_0/k_B T}}{1 + e^{-h\tilde{\gamma}_e H_0/k_B T}} \approx \frac{h\tilde{\gamma}_e H_0}{2k_B T}\,, \tag{4}$$

where k_B is Boltzmann's constant and $\tilde{\gamma}_e$ is the electron gyromagnetic ratio (28 024.95 MHz/T). In other words, a Curie-like local spin susceptibility is obtained, as in the case of an isolated electronic moment. (The last term in Eq. (4) is valid at high temperatures, which in our experimental conditions corresponds to $T > 4$ K.) Combining with Eq. (3) yields [10]

$$\mathcal{K} = \frac{m_{\rm th}}{T} = \frac{1}{T}\left(\frac{-h\tilde{\gamma}_e(A_{\perp}\sin^2\theta + A_{\|}\cos^2\theta)}{4k_B\tilde{\gamma}_{\mu}}\right). \tag{5}$$

Figure 1(a) displays the typical signal in our heavily doped n-type Si:P samples, shown for Si:P-1 at $T = 100$ K, where H_0 is applied parallel to a $\langle 100 \rangle$ crystallographic axis. The data are displayed in a reference frame rotating at $\approx$5 MHz above the Larmor precession frequency of the diamagnetic signal. Note the beating which shows there are two clearly resolved frequencies which may be seen more clearly in the Fourier transform shown in Fig. 1(b). The frequency labeled ν_0 was found to be independent of temperature and attributed primarily to diamagnetic Mu_T^-. The second frequency, which we have labeled as ν_{BC}, has not to our knowledge been seen previously in semiconductor samples. We can unambiguously assign this line to Mu_{BC}^0 because of the sign and magnitude of the frequency shift along with its dependence on crystal orientation. For example, the magnitude of the shift in the sample with the lowest carrier concentration (Si:P-1) is very close to that predicted from using the measured hyperfine parameters of Mu_{BC}^0 in intrinsic silicon. Note also the sign of the shift, and therefore the induced hyperfine field on the muon, is negative—which is unusual for a paramagnetic center. This occurs for Mu_{BC}^0 because of core polarization effects and the fact that the muon is at a node in the positive spin density distribution [11]. Final confirmation comes from the orientation dependence of the ν_{BC} line(s). As shown in Fig. 1(c) for the Si:P-4 sample, when $H_0 \| \langle 110 \rangle$ rather than $\langle 100 \rangle$, the ν_{BC} line splits as predicted for the $\langle 111 \rangle$ axially symmetric hyperfine interaction of Mu_{BC}^0. This is easily understood by considering either Eqs. (2) or (3). When $H_0 \| \langle 100 \rangle$, there are four equivalent sites for Mu_{BC}^0, all at $\theta = 54.7°$; hence, one frequency is expected. On the other hand, when $H_0 \| \langle 110 \rangle$, half of the Mu_{BC}^0 centers are described by $\theta = 35.3°$ and the other half by $\theta = 90°$; hence, two signals corresponding to Mu_{BC}^0 are now expected and indeed observed.

We now consider the temperature dependence of $\mathcal{K} = (\nu_o - \nu_{BC})/\nu_o$ for Si:P-1, Si:P-2, and Si:P-3 with $H_0 \| \langle 100 \rangle$. These data are plotted in Fig. 2. The inset shows $\mathcal{K}T$ vs T, which should be temperature independent for each sample if the Curie-like theoretical behavior [Eq. (5)] is obeyed. Also shown for each sample are fits assuming the expression $\mathcal{K} = m_{exp}/T$ [12]. Using the hyperfine parameters for Mu_{BC}^0 in intrinsic Si [13] ($A_\| = -16.82$ MHz, $A_\perp = -92.59$ MHz), one predicts from Eq. (5) that $m_{th} = 0.1670$ K, corresponding to the dashed line in Fig. 2. As seen in Fig. 2, the agreement between m_{th} and m_{exp} is very good in Si:P-1 [$m_{exp} = 0.1666(4)$ K], the sample with the lowest dopant concentration. However, there is a significant reduction ($\approx$13%) for the Si:P-2 sample [$m_{exp} = 0.144(6)$ K] and a $\approx$32% reduction of the hyperfine parameter at the highest dopant level [$m_{exp} = 0.11(1)$ K] [14]. This indicates that the spin density distribution around the muon is more delocalized at the higher carrier concentrations. We attribute this to the charge screening from the free carriers. Such a change in the electronic structure for a deep level impurity has not been reported in a semiconductor to our knowledge. Perhaps no other technique is capable of characterizing the electronic structure of the same

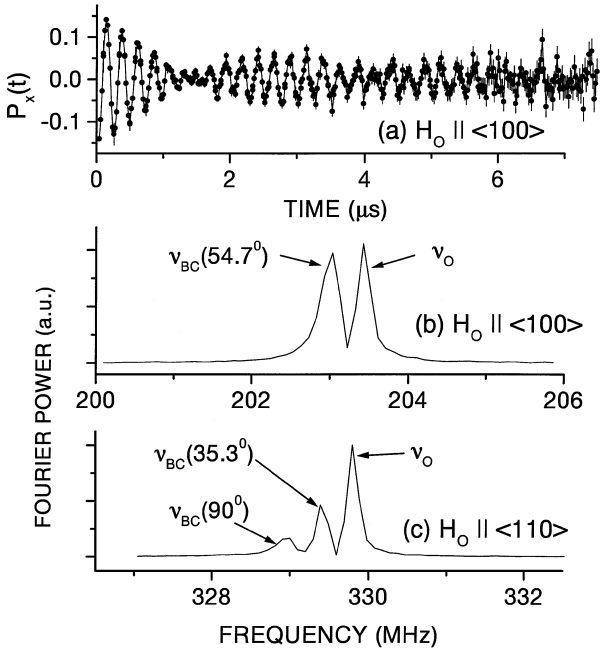

FIG. 1. (a) The TF-μSR spectrum in Si:P-1 at $T = 100$ K and $\mathbf{H}_0 \simeq 1.5\ T \| \langle 100 \rangle$. The data and fit (solid line) are shown for convenience in a reference frame rotating about 5 MHz above ν_0. (b) The Fourier transform of the above TF-μSR signal. (c) The Fourier transform for the Si:P-4 sample with $\mathbf{H}_0 \simeq 2.5\ T \| \langle 110 \rangle$. Mu_{BC}^0 gives rise to two lines in this orientation.

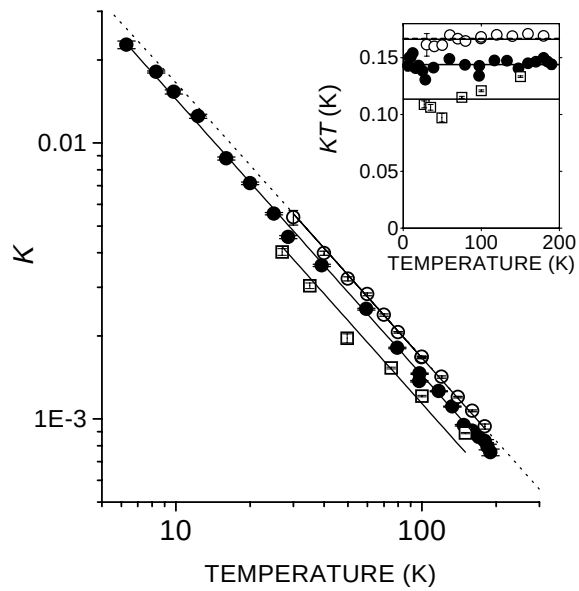

FIG. 2. The normalized frequency shift $\mathcal{K}$ (main plot) and $\mathcal{K}T$ (inset) as a function of temperature. In both the main plot and the inset, the open circles, closed circles, and open squares indicate data for Si:P-1, Si:P-2, and Si:P-3, respectively, while the solid lines are fits to the data and the dashed line is a theoretical prediction (see text).

impurity over such a wide range of carrier concentrations (7 orders of magnitude). Furthermore, it is worth noting that this effect should not be limited to muonium centers, but is likely quite a general phenomenon in the case of materials with high carrier concentrations.

The observation that the local susceptibility so close to Curie-like implies that the Kondo spin screening of the muonium by the conduction electrons is small at these temperatures or, in other words, the effective Kondo temperature is much less than a few K.

Finally, we remark on the temperatures at which the Mu^0_{BC} center is observed. In the most lightly doped of the three samples, i.e., Si:P-1, the Mu^0_{BC} is not observed until about 30 K. The explanation for this is that significant thermal ionization of the phosphorous donors does not occur in this *nonmetallic* sample below this temperature. Hence, the free electron concentration is significantly smaller, the spin exchange rate is accordingly reduced, and we are not in the "rapid fluctuation" regime required for direct observation of the transverse-field signal. Contrast this with the *metallic* Si:P-2 sample, where the high free electron concentration required for fast spin exchange is present even at very low temperatures. Note also that the signature for Mu^0_{BC} persists until $\approx$200 K, while in high resistivity–low doped Si, the same center ionizes [2] by $\approx$120 K and cannot be seen directly above this temperature. Hence, it is quite certain that reversible charge state changes, i.e., $Mu^0_{BC} \leftrightarrow Mu^+_{BC}$, are occurring between 120 and 200 K. (Above 200 K, it is likely that Mu^0_{BC} converts to Mu^-_T [15].) These results are consistent with the interpretation of radio-frequency μSR data and longitudinal-field depolarization rates in Si:P doped at intermediate concentrations [15,16]. Last, the observation of Mu^0_{BC} confirms the existence of a large energy barrier for the BC to *T* site change (the *T* site is the stable one for Mu^-).

In conclusion, we have observed bond-centered muonium in heavily doped *n*-type Si:P, indicating that Mu^0_{BC} is metastable with respect to a transition to the negative charge state, Mu^-_T. Under these conditions Mu^0_{BC} undergoes very rapid spin exchange which averages the muon hyperfine interaction. Nevertheless, an unambiguous identification of Mu^0_{BC} in such a metallic environment is possible using transverse-field μSR to induce a giant frequency shift resulting from the large local spin susceptibility of muonium. Our most important observation is the reduction in the hyperfine parameter as the carrier concentration increases. Such an effect is evidence that the electronic structure of Mu^0_{BC} changes substantially as a result of charge screening by the free carriers. This is likely to be a general phenomenon for deep level impurities in the high carrier concentration limit.

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[1] K. H. Chow, B. Hitti, and R. F. Kiefl, in *Identification of Defects in Semiconductors*, edited by M. Stavola (Academic Press, New York, 1998), p. 137.
[2] Good reviews are B. D. Patterson, Rev. Mod. Phys. **60**, 69 (1988); R. F. Kiefl and T. L. Estle, in *Hydrogen in Semiconductors*, edited by J. Pankove and N. M. Johnson (Academic, New York, 1990), p. 547.
[3] Some useful reviews are *Hydrogen in Semiconductors*, edited by J. Pankove and N. M. Johnson (Academic Press, New York, 1990); S. J. Pearton, J. W. Corbett, and M. Stavola, *Hydrogen in Crystalline Semiconductors* (Springer, New York, 1992); S. M. Myers *et al.*, Rev. Mod. Phys. **64**, 559 (1992).
[4] K. H. Chow *et al.*, Phys. Rev. B **47**, 16 004 (1993).
[5] K. H. Chow *et al.*, Phys. Rev. B **50**, 8918 (1994).
[6] The charge state of an impurity in highly conductive material is meaningful only if the electronic disturbance is localized within the screening length r_s. In heavily doped Si, $r_s \simeq 30$ Å.
[7] C. P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, New York, 1990), p. 521.
[8] R. F. Kiefl *et al.*, Phys. Rev. B **32**, 530 (1985).
[9] Erik S. Sorensen and Ian Affleck, Phys. Rev. B **53**, 9153 (1996).
[10] In the special case of isotropic muonium $A_\parallel = A_\perp = A_\mu$, this equation reduces to the result obtained by M. Senba, Phys. Rev. A **50**, 214 (1994).
[11] S. Estreicher, Phys. Rev. B **36**, 9122 (1987); S. Vogel *et al.*, J. Phys. Condens. Matter **1**, 4729 (1989); C. G. Van de Walle, Phys. Rev. Lett. **64**, 669 (1990).
[12] The fits are obtained by calculating the mean value of $\mathcal{K}T$ for each sample, i.e., $m_{\rm exp} = \langle \mathcal{K}T \rangle$.
[13] K. W. Blazey *et al.*, Phys. Rev. B **27**, 15 (1983).
[14] There may be a deviation from a $1/T$ dependence in the Si:P-3 sample above $\approx$100 K. Nevertheless, at all temperatures, $\mathcal{K}$ monotonically decreases with increasing dopant concentration, hence verifying that the hyperfine interaction is also decreasing.
[15] B. Hitti *et al.*, Phys. Rev. B **59**, 4918 (1999); B. Hitti *et al.*, Hyperfine Interact. **105**, 321 (1997); S. R. Kreitzman *et al.*, Phys. Rev. B **51**, 13 117 (1995).
[16] R. L. Lichti, in *Hydrogen in Semiconductors, II*, edited by N. Nickel (Academic Press, New York, 1999), p. 311.
[17] H. Alloul and P. Dellouve, Phys. Rev. Lett. **59**, 578 (1987); H. Alloul and P. Dellouve, J. Phys. (Paris) **C8**, 1185 (1988).