PHYSICAL REVIEW B **73**, 081203(R) (2006)

Muonium in InSb: Shallow acceptor versus deep trap or recombination center

V. G. Storchak,[1,*] D. G. Eshchenko,[2] J. H. Brewer,[3] S. P. Cottrell,[4] and R. L. Lichti[5]
[1]*Russian Research Center "Kurchatov Institute," Kurchatov Square 46, Moscow 123182, Russia*
[2]*Physik-Institut der Universität Zürich, CH-8057 Zürich, Switzerland*
[3]*Canadian Institute for Advanced Research and Department of Physics and Astronomy, University of British Columbia, Vancouver, British Columbia V6T 1Z1, Canada*
[4]*ISIS Facility, Rutherford Appleton Laboratory, Oxfordshire OX11 OQX, United Kingdom*
[5]*Physics Department, Texas Tech University, Lubbock, Texas 79409-1051, USA*
(Received 23 January 2006; published 22 February 2006)

The bound state of a muonium atom has been detected in both *n*-type and *p*-type InSb using a high-field μSR technique. The hyperfine constant obtained for this isotropic center ($A_T = 2464 \pm 1$ MHz), roughly half that of a Mu atom in vacuum, is characteristic of deep level Mu^0 centers at tetrahedral interstitial sites in other cubic semiconductors, which typically ionize above 250 K. In contrast, the Mu^0 signal in InSb begins to disappear near 20 K, which is more characteristic of ionization of a shallow level impurity. The charge-state dynamics of Mu in InSb can be understood in terms of the predicted shallow acceptor behavior for H in InSb versus a deep hole trap or recombination center, rather than as ionization via electron promotion to the conduction band.

DOI: 10.1103/PhysRevB.73.081203 PACS number(s): 72.20.Jv, 36.10.Dr, 71.55.Eq, 76.75.+i

Electrically active impurities in semiconductors can be characterized as shallow or deep donors or acceptors, with the deep-level impurities acting as electron or hole traps or as recombination centers, depending on relative rates of carrier capture and ionization processes involving that impurity. Hydrogen is a very common impurity in semiconductors, and has been demonstrated or predicted to take on each of these roles in one material or another. It is most often a deep-level compensating defect, meaning that it acts as an acceptor in *n*-type materials and as a donor in a *p*-type host. Hydrogen occupies different interstitial sites as an ionized donor (H^+) or acceptor (H^-), and one of these sites is typically also home to the lowest energy neutral charge state. The lattice relaxation (and Coulombic energy in polar semiconductors) typically makes H a "negative-*U*" defect with the donor level H(+/0) lying above the acceptor level H(0/−) in inverted order, and the neutral charge state is never preferred in thermal equilibrium.[1,2] For normal ordering, these thermodynamic defect levels represent the Fermi energy at which the dominant equilibrium charge state would change for the donor or acceptor site, respectively.

Hydrogen is often quite mobile in these materials and reacts with various other impurities or defects, thereby modifying the associated electrical activity of those defects. While this chemical activity of hydrogen is well studied, it makes direct observation of the electrical behavior of an isolated hydrogen impurity extremely difficult. However, extensive experiments on the very light and short-lived isotope muonium,[3,4] or Mu, in which a positive muon replaces the proton, have provided considerable information on the sites, charge states, and dynamics of the associated carrier capture and ionization processes in numerous semiconductors where the equivalent data for hydrogen itself are not available. Despite the factor of nine in atomic mass between Mu and H, any purely electronic property is, for all practical purposes, identical. Thus the electrical activity obtained for Mu should faithfully reproduce that expected for H. In this paper we report the first observation of a neutral Mu center and its charge state dynamics in InSb. These results are discussed in relation to the predicted properties of hydrogen in this narrow-gap semiconductor and features common to Mu in other III-V compounds.

Recent theoretical arguments,[5] based on detailed calculations for a few materials, place the crossover from H^+ to H^- as the stable state at a common energy level H(+/−) with respect to vacuum, independent of the host, and provide an easy method to predict electrical properties of H or Mu. The band alignments in this reference place the H(+/−) level within the valence band of InSb, and thus predict that H should be a shallow acceptor in this material. If one accepts that H(+/−) is universal, then a similar conclusion can be drawn from earlier and slightly different results for valence band offsets in III-V and II-VI compounds[6] and the calculated position of H(+/−) in several oxides.[7] Similar arguments successfully predict shallow donor behavior of Mu where theory has H(+/−) conduction-band resonant, as for InN.[8]

In a muon spin rotation (μ^+SR) experiment, the time-dependent spin polarization of positive muons stopped in the sample is revealed in a spectrum accumulated from many individual μ^+ decay events. As the 4 MeV muon slows to about 10 keV, inelastic μ^+ scattering produces mainly atomic excitations and ionizations. At lower energies, collective excitations and charge exchange become important. In semiconductors, the μ^+ can pick up an e^- to form a Mu atom which then interacts with the host material as would an H atom. The muon can thermalize as either a neutral Mu atom (*prompt* formation of Mu^0) or a positive ion (Mu^+), leaving behind an ionization track of liberated electrons and holes. An electron from this track may subsequently reach the prompt Mu^+ and form Mu^0 within the time range of a μ^+SR experiment[9] (*delayed* formation of Mu^0).

In covalent diamond or zincblende structured semiconductors, a bond-centered (BC) site is the stable location for Mu^{+}[10] and the largest interstitial "cage" region of the lattice, the T site, is the stable location for a Mu^{-} ionic center.[11] Both locations can support a neutral center; when it is seen, Mu^{0}_{BC} is normally the lowest energy neutral state.[12] The charge state properties make the T site the Mu acceptor location and the BC site the preferred location for a Mu donor. For more ionic zincblende compounds, the two inequivalent T sites can separately take on donor and acceptor characteristics: T_{III} with anion nearest neighbors becomes the acceptor site, and T_V with cation neighbors may provide a second (meta)stable donor location.

Investigations of the Mu^0 formation processes in Si,[13] GaAs,[14,15] and GaP,[16] using an applied electric field to modify the capture of track electrons by the stopped μ^+, demonstrate that Mu^{0}_{BC} is formed initially as an intermediate state in which the electron is very weakly bound, whereas Mu^{0}_{T} is probably formed epithermally. Vastly different hyperfine interactions allow easy identification of the T and BC Mu^0 centers in spin precession spectra, while Mu^{+}_{BC} and Mu^{-}_{T} yield indistinguishable (diamagnetic) precession signals.

The muonium hyperfine frequency A is a measure of the electron spin density at the muon which provides information on the electronic structure of the Mu^0 center. The Mu^{0}_{T} center is essentially a trapped atom and has an isotropic hyperfine interaction with a hyperfine frequency A_T about half that of a free Mu atom in vacuum (A_0=4463 MHz). The MU^{0}_{BC} center has reacted with the host lattice and has a small anisotropic hyperfine interaction oriented along the ⟨111⟩ bond directions ($A_{BC} \sim A_0/50$). In many semiconductors, both centers are associated with energy levels lying quite deep in the gap. In Si, for instance, Mu^{0}_{BC} occupies a donor level at $E_c - 0.21$ eV based on observed ionization dynamics.[17] The singly occupied energy level for Mu^{0}_{T} lies much lower, putting a T-site donor level deep in the valence band. The binding energy of the second electron (Mu^{-}_{T}) is much less and often puts the T-site acceptor level in the gap. In *n*-type Si, an observed rapid, electron exchange cycle between Mu^{-}_{T} and Mu^{0}_{T} places the T(0/−) acceptor level near mid-gap.[18] In *n*-type GaAs, Mu_T functions as a recombination center,[19] rather than as either an electron or hole trap. For the narrow-gap semiconductor InSb, one would not anticipate that any deep muonium level should fall within the band gap, especially given the theoretical prediction of shallow acceptor behavior.

Time-differential μSR experiments were performed at high magnetic fields (up to 7 T) on the M15 surface muon channel at TRIUMF using the HiTime apparatus. The data were recorded with a nominal time-bin resolution of 50 ps; the actual time resolution for this spectrometer is ~150 ps. We studied two InSb crystals, both well compensated by the addition of $\sim 10^{15}$ cm^{-3} Zn impurities; one was slightly *n* type and the other slightly *p* type at net concentrations of approximately 10^{12} cm^{-3}.

For a static Mu atom in III-V compounds, determination of the hyperfine frequency requires a strong magnetic field in order to decouple the electron spin from nuclear magnetic moments. Our high-field experiments on *n*- and *p*-type InSb reveal several signals which correspond to a paramagnetic muonium state (Mu^0) and a diamagnetic state (either Mu^+ or Mu^-). To the best of our knowledge, this is the first observation of a neutral muonium center in InSb; previous measurements[3] showed no paramagnetic center(s).

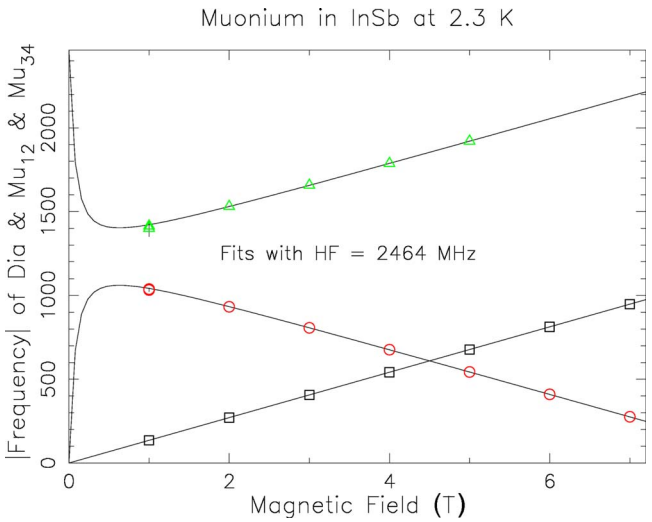

FIG. 1. (Color online) Magnetic field dependences of the paramagnetic Mu frequencies ($|\nu_{12}|$: circles and ν_{34}: triangles) and the diamagnetic frequency (squares) in 10^{12} cm^{-3} *n*-type InSb at 2.3 K. Solid lines for the Mu^0 frequencies represent a fit assuming an isotropic hyperfine interaction.

Figure 1 shows the magnetic field dependences of the Mu^0 spin precession frequencies $|\nu_{12}|$ and ν_{34}, which in high field correspond to muon spin flips with the Mu^0 electron spin "down" and "up," respectively, along with the diamagnetic frequency, which is taken to be positive. At the highest fields (above 5 T) the amplitude of the ν_{34} signal becomes too small to follow above about 2 GHz. Fitting these frequencies to the Breit-Rabi Hamiltonian shows that the paramagnetic spectrum at 2.3 K corresponds to a Mu_0 center with an *isotropic* hyperfine interaction $A = 2464 \pm 1$ MHz. Although not investigated to the same extent, identical spectra are present with similar intensities in the *p*-type InSb sample.

The large measured value of the hyperfine interaction is characteristic of Mu^{0}_{T} as observed in other III-V semiconductors, such as GaAs and GaP, and in group-IV semiconductors Si, Ge, and C (diamond).[3] Such a large value of A is strong evidence for a highly localized Mu^0 center: the mean radius of the electronic wave function is typical of an ordinary isolated Mu atom trapped in a solid. We therefore propose a T-site assignment based on behavior common to other cubic semiconductors.

The electron binding energy of such a Mu center is quite large; thus its $1s^1$ energy level must lie deep below the conduction band minimum, a rough estimate being ~1 eV.[20] Such a high value does not allow this level to be accommodated within the extremely narrow gap of InSb (0.24 eV at 80 K). Then one has to accept that this energy level lies deep in the valence band.

Figure 2 shows the temperature dependence of the disappearance rate T_2^{-1} of the paramagnetic signal in InSb at 3 T. Above about 60 K no Mu^0 signal was detectable. Within

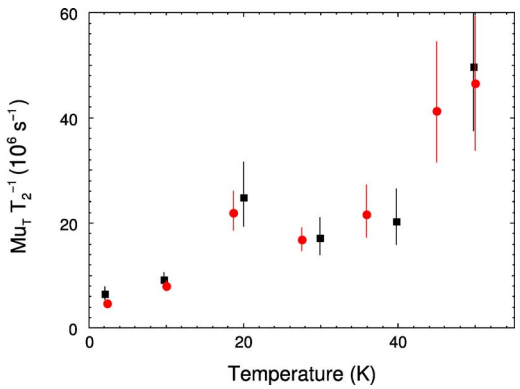

FIG. 2. (Color online) Temperature dependence of the exponential relaxation rate of the Mu^0 signal in n-InSb (circles) and p-InSb (squares) in a transverse magnetic field of 3 T.

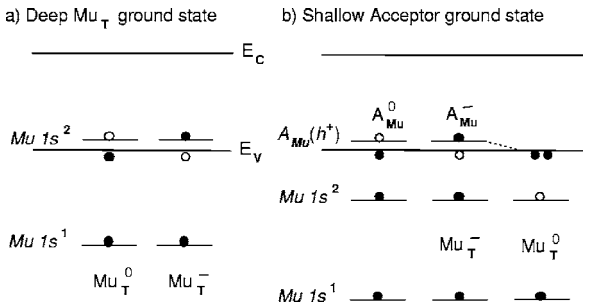

FIG. 3. Energy levels for Mu_T (a) as a deep defect or (b) with a shallow-acceptor (A_{Mu}) ground state. Electron (hole) occupancies are shown for each charge state.

statistical uncertainties, n-type and p-type samples have the same T_2^{-1} at the same T. Although the apparent relaxation peak near 20 K suggests that more than one process may contribute, the progressive increase in T_2^{-1} with increasing temperature suggests that T_2 is simply the lifetime of the Mu_T^0 state.

In other semiconductors, the highly localized Mu^0 centers disappear above 250 K; our experiments show that the Mu_T^0 signal in InSb starts to disappear at about 20 K. This temperature is more typical of thermal ionization of the shallow donor Mu^0 states observed in several compounds,[21] which are characterized by extremely small hyperfine constants ($A \sim 10^{-4} A_0$).

Fitting $T_2^{-1}(T)$ to a simple Arrhenius law yields an activation energy $E_a = 6.5 \pm 1.3$ meV, equivalent to $k_B T$ at 75 K. Neither this E_a nor the temperature range for Mu^0 disappearance in InSb are consistent with *thermal ionization* of an atomic-like Mu^0 center, as discussed above. The most straightforward explanation for this transition, based on common features for Mu in III-V compounds, would be thermal promotion of an electron out of the valence band onto the Mu_T impurity to form Mu_T^-. This is equivalent to *hole ionization* as expected for a shallow acceptor, and thus would seem to be consistent with theoretical predictions.[5] However, the situation is not that simple. The difficulty is that the large hyperfine constant implies a highly localized atomic-like Mu^0, and is *not consistent* with an effective-mass shallow acceptor.

If the above interpretation involving h^+ ionization of an atomic-like Mu_T^0 is correct, the fact that the Mu^0 signal disappears at low temperature implies that the acceptor level for a localized Mu impurity happens to fall just above the valence-band edge in InSb. This situation is depicted in Fig. 3(a).

Alternatively, if the shallow-acceptor prediction[5] is correct, the energy level for the Mu_T^- $1s^2$ configuration has to be below the top of the valence band, as in Fig. 3(b). The observed atomic-like Mu_T^0 then requires an h^+ in this valence band-resonant localized level. In order to form the predicted shallow-acceptor level for A_{Mu}, the muonium defect needs to be in its negative charge state; the localized Mu_T^- is equivalent to the ionized shallow acceptor A_{Mu}^-. The only way to directly obtain the neutral shallow acceptor A_{Mu}^0 from the observed Mu_T^0 is for the h^+ to transfer from the Mu $1s^2$ level to the weakly bound state associated with the shallow acceptor. This weakly bound h^+ implies that A_{Mu}^0 should have a hyperfine constant $\leqslant 10^{-3}$ times the value observed experimentally.

One should, however, keep in mind an important difference between the ways hydrogen and muonium are introduced into the sample and then detected. Hydrogen is typically introduced chemically and has plenty of time to reach thermodynamic equilibrium. Muonium, by contrast, is formed during or immediately following high energy μ^+ implantation[22] and only those states reached on the microsecond time scale of the muon lifetime can be studied. This circumstance may permit reconciliation of the observed Mu features with the predicted state by assuming that Mu_T^0 may simply not have had sufficient time to fully thermalize. The final steps in Mu thermalization would be capture of an e^- from the valence band and localization of Mu_T into the T_{In} site as Mu^- with the subsequent formation of a shallow A_{Mu} center with its charge state depending on whether or not the displaced h^+ remains bound to Mu^-.

An alternative way to form Mu_T^0 is for the muon to stop in a T_{Sb} site as Mu^+ followed by capture of an e^-, presumably through an intermediate weakly bound state in analogy to Mu_{BC}^0 formation in GaAs and GaP (Refs. 14, 16, and 22). A technique to distinguish this from prompt Mu^0 formation is to apply an electric field; unfortunately, our InSb samples do not hold even very weak electric fields. Another characteristic feature of this formation process would be an increased Mu^0 fraction in a high magnetic field due to electron freezeout.[23] However, both the diamagnetic and Mu^0 amplitudes in InSb are independent of field up to 7 T at $T = 2.3$ K, consistent with epithermal Mu_T^0 formation.

Instead of h^+ ionization, the disappearance of Mu_T^0 might be by carrier capture or by a charge-transfer interaction with shallow dopants, as has been proposed for GaP.[24] Since our InSb samples contain $\sim 10^{15}$ cm^{-3} of both donors and acceptors, charge transfer could yield Mu_T^- if the interaction were with either a neutral donor or an ionized acceptor. Binding energies for shallow donors and Zn acceptors in InSb are $\leqslant 1$ and ~ 10 meV, respectively.[25] If the relaxation in Fig. 2 is treated as carrier capture, then $T_2^{-1} \sim N v_o \sigma$, where N is the dopant concentration and v_o is a carrier velocity, and one

obtains a cross section of $\sigma \sim 10$ Å^2, reasonably consistent with such interactions. Given the small gap of InSb, a deep-level Mu_T acceptor would act either as a hole trap (in its dominant negative charge state) or as a recombination center, depending on exactly where its $T(0/-)$ energy level lies.

In conclusion, we report the observation of a neutral muonium center in the narrow-gap semiconductor InSb. The observed hyperfine interaction implies a deep localized Mu_T^0 state rather than the theoretically predicted shallow Mu acceptor. Taken at face value, this observation contradicts current theory; however, we also present a possible scenario involving a long-lived, metastable, epithermally formed Mu^0 state which may still be consistent with theory. In any event, the existing data on muonium do not support the prediction of shallow acceptor properties for hydrogen in InSb. We discuss several possible mechanisms for the low-temperature disappearance of the observed deep Mu_T^0 state in addition to hole ionization. Additional experiments on the charge dynamics for Mu centers in InSb may resolve the question of whether the Mu isotope of hydrogen eventually forms the predicted shallow acceptor ground state, or if it remains a deep hole trap or recombination center.

This work was supported by the Canadian Institute for Advanced Research, the Natural Sciences and Engineering Research Council of Canada, the US National Science Foundation, the Welch Foundation, and the Royal Society of London.

*Electronic address: storchak@stor.polyn.kiae.su

[1] C. G. Van de Walle, in *Hydrogen in Semiconductors*, edited by J. Pankove and N. M. Johnson, Semiconductors and Semimetals Vol. 34 (Academic, New York, 1990).

[2] C. Herring, N. M. Johnson, and C. G. Van de Walle, Phys. Rev. B **64**, 125209 (2003).

[3] B. D. Patterson, Rev. Mod. Phys. **60**, 69 (1988).

[4] R. L. Lichti, in *Hydrogen in Semiconductors, II*, edited by N. Nickel, Semiconductors and Semimetals Vol. 61 (Academic, San Diego, 1999).

[5] C. G. Van de Walle and J. Neugebauer, Nature (London) **423**, 626 (2003).

[6] S-H Wei and A. Zunger, Appl. Phys. Lett. **72**, 2011 (1998).

[7] C. Kilic and A. Zunger, Appl. Phys. Lett. **81**, 73 (2002).

[8] E. A. Davis, S. F. J. Cox, R. L. Lichti, and C. G. Van de Walle, Appl. Phys. Lett. **82**, 592 (2003).

[9] V. G. Storchak, J. H. Brewer, and D. G. Eshchenko, Appl. Magn. Reson. **13**, 15 (1997).

[10] K. H. Chow, B. Hitti, R. L. Lichti, and S. F. J. Cox, Physica B **340-342**, 280 (2003).

[11] K. H. Chow, R. F. Kiefl, W. A. MacFarlane, J. W. Schneider, D. W. Cooke, M. Leon, M. Paciotti, T. L. Estle, B. Hitti, R. L. Lichti, S. F. J. Cox, C. Schwab, E. A. Davis, A. Morrobel-Sosa, and L. Zavieh, Phys. Rev. B **51**, R14762 (1995).

[12] S. K. Estreicher, Mater. Sci. Eng., R. **14**, 319 (1995).

[13] V. Storchak, S. F. J. Cox, S. P. Cottrell, J. H. Brewer, G. D. Morris, D. J. Arseneau, and B. Hitti, Phys. Rev. Lett. **78**, 2835 (1997).

[14] D. G. Eshchenko, V. G. Storchak, and G. D. Morris, Phys. Lett. A **264**, 226 (1999).

[15] D. G. Eshchenko, V. G. Storchak, J. H. Brewer, and R. L. Lichti, Phys. Rev. Lett. **89**, 226601 (2002).

[16] V. G. Storchak, D. G. Eshchenko, R. L. Lichti, and J. H. Brewer, Phys. Rev. B **67**, 121201(R) (2003).

[17] S. R. Kreitzman, B. Hitti, R. L. Lichti, T. L. Estle, and K. H. Chow, Phys. Rev. B **51**, 13117 (1995).

[18] B. Hitti, S. R. Kreitzman, T. L. Estle, E. S. Bates, M. R. Dawdy, T. L. Head, and R. L. Lichti, Phys. Rev. B **59**, 4918 (1999).

[19] K. H. Chow, B. Hitti, R. F. Kiefl, S. R. Dunsiger, R. L. Lichti, and T. L. Estle, Phys. Rev. Lett. **76**, 3790 (1996).

[20] V. N. Abakumov, V. I. Perel, and I. N. Yassievich, *Non-radiative Recombination in Semiconductors*, edited by V. M. Agranovich and A. A. Maradudin, Modern Problems in Condensed Matter Sciences (North-Holland, Amsterdam, 1991), Vol. 33, pp. 1–320.

[21] S. F. J. Cox, J. Phys.: Condens. Matter **15**, R1727 (2003).

[22] V. G. Storchak, D. G. Eshchenko, and J. H. Brewer, J. Phys.: Condens. Matter **16**, 4761 (2004).

[23] V. G. Storchak, D. G. Eshchenko, J. H. Brewer, B. Hitti, R. L. Lichti, and B. A. Aronzon, Phys. Rev. B **71**, 113202 (2005).

[24] R. L. Lichti, K. H. Chow, Y. G. Celebi, E. A. Davis, B. Hitti, and S. F. J. Cox, Physica B **326**, 167 (2003).

[25] *Handbook Series on Semiconductor Parameters*, edited by M. Levinshtein, S. Rumyantsev, and M. Shur (World Scientific, Singapore, 2000), Vol. 1.