Demonstration of the effect of uniaxial stress on the electronic structure of bond-centered muonium in Si

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We demonstrate that compressive uniaxial stress modifies the electronic structure of bond-centered muonium (Mu^0_{BC}) in Si. The stress was applied along the ⟨100⟩ direction of the sample and results in a significant change in the hyperfine parameters of Mu^0_{BC}.

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Muonium [$Mu=(\mu^+e^-)$, spin 1/2] centers in semiconductors are defects which have electronic structures essentially identical to those of hydrogen. These similarities have led to the frequent use of Mu as an experimental analog for the *isolated* states of hydrogen in semiconductors, where the latter is widely recognized as a very important interstitial impurity in these technologically relevant materials.[1–12]

In high resistivity crystalline silicon, two neutral (i.e., paramagnetic) muonium centers, now commonly labeled as Mu^0_{BC} and Mu^0_T in the literature, are formed when positive muons are implanted into the sample at low temperatures. About 37% of the implanted muons form Mu^0_{BC} while ≈61% end up as Mu^0_T (a small fraction of the muons also end up as diamagnetic centers, i.e., likely Mu^+ or Mu^-).[13] The electronic structures of these centers are now well characterized.[14] Mu^0_T has an isotropic muon-electron hyperfine parameter about half that of the vacuum state and is believed to be diffusing between tetrahedral interstitial sites. The other center Mu^0_{BC} is located close to a Si-Si bond-center (BC) position.[15] It is immobile on the time scale of the muon lifetime (2.2 μs) and it ionizes at ≈150 K. As a consequence of its location, the hyperfine interaction of Mu^0_{BC} is axially symmetric about a ⟨111⟩ crystalline axis and is described by two parameters $A_\parallel$ and $A_\perp$ which are approximately an order of magnitude smaller than the contact interaction for Mu^0_T, i.e., A_μ ($A_\parallel=-16.82$ MHz, $A_\perp=-92.59$ MHz).[1,14,16]

In this paper, we address the following question: Will a reasonable amount of uniaxial stress produce measurable changes in the hyperfine interaction of Mu^0_{BC} in Si? There are a number of reasons for establishing whether stress produces observable effects in the local electronic structure of Mu^0_{BC}. The first motivation is one of scientific curiosity. Holzschuh *et al.*[17] have measured the hydrostatic pressure dependence of the hyperfine parameter A_μ for Mu^0_T in Si at 273 K, but found no significant pressure dependence in A_μ up to ≈1500 bar (0.15 GPa). [Using the bulk modulus[18] of Si (0.988×10^{11} N/m^2) this pressure corresponds to a compressive strain of $\delta a/a\approx500$ ppm.] In the case of Mu^0_{BC}, it is also not clear whether a reasonable amount of applied stress will have any affect since in order to accomodate this defect at the BC position, there is already significant stretching of the Si-Si bond.[15,19] It is true that the hyperfine parameters of Mu^0_{BC} change with temperature, but it was argued by the authors responsible for these studies[20,21] that the observed monotonic variation implies that lattice dilation/ expansion[22] effects are *not* responsible. On the other hand, due to the strong coupling between the lattice and the muonium state located at the BC position, we anticipate the local strain could induce a large change in the hyperfine parameters of Mu^0_{BC}. Except for our current experiments, described below, we are not aware of any reported measurements on the effects of externally applied stress on the hyperfine parameters of Mu^0_{BC}.

Another reason for our experiments is that successful observation of a stress-related effect on the hyperfine parameters of Mu^0_{BC} could prove interesting to theorists calculating the details of muonium (or hydrogen)-lattice interactions. The properties, i.e., how the crystal parameters change, of conventional semiconductors under stress are well understood. Hence, a study of the behavior of the hyperfine parameters of muonium centers in semiconductors could provide a stringent test of theoretical models which are dedicated to estimating hydrogen or muonium hyperfine parameters. A third reason is that future experiments on muonium in semiconductors may be focussed on investigating the dynamical aspects of muonium in a strained lattice, including formation probabilities of muonium, transition rates for interconversion between states, etc. Hence, it would be useful to have a means of verifying that stress has been introduced into the material at the microscopic level: detecting stress related changes in hyperfine parameters of certain muonium states (e.g., Mu^0_{BC}) could be such a means.

The experiments described in this paper were performed at TRIUMF. Positive muons of nominal momentum ≈30 MeV/c and spin polarization close to 100% are implanted into the sample. The sample studied is a slightly *p*-type silicon sample obtained from TOPSIL with a ⟨100⟩ face and impurity concentration 3×10^{11} cm^{-3}. The sample is rectangular with dimensions ≈15 mm×9 mm×2 mm (thickness). The two 15 mm×2 mm surfaces of the sample are perpendicular to a ⟨110⟩ direction, while the two 15 mm×9 mm faces are perpendicular to a ⟨100⟩ direction.

The uniaxial compressive stress was applied perpendicular to **H** and along one of the ⟨110⟩ directions (i.e., the stress is applied to the two 15 mm×2 mm surfaces of the sample). Figure 1 summarizes the experimental situation. Since our

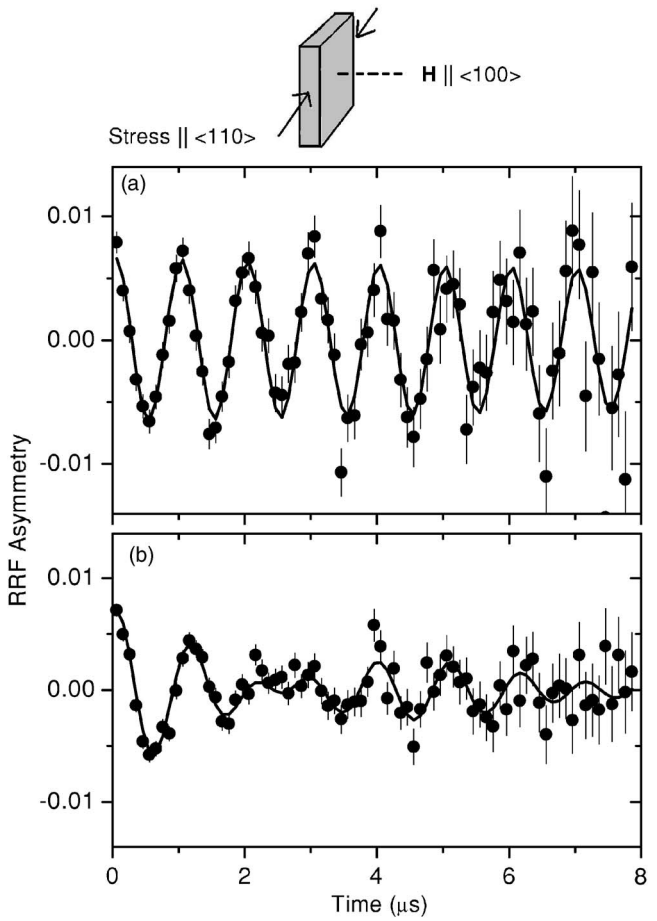

FIG. 1. The LF-μSR precession signal due to Mu_{BC}^0 at 17.5 K (a) in the absence of applied stress and (b) with an applied uniaxial compressive stress. The data are displayed in a rotating reference frame (RRF) with a reference frequency of 18.0 MHz. The solid lines are fits to the data as described in the text. The schematic [above panel (a)] summarizes the directions of the applied stress and the magnetic field **H** with respect to the rectangular sample.

goal is to perform a proof-of-principle demonstration that uniaxial stress can affect the Mu_{BC}^0 hyperfine parameters, we used a relatively simple arrangement for applying stress to the sample. The silicon was placed in a groove, machined to the size of the sample, in a piece of copper. A snug fit was obtained by placing sufficient pieces of thin aluminum foil (thickness 0.01 mm) between the sample and the copper groove. Upon cooling the system to 17.5 K, the different thermal expansion coefficients between the metals and the Si result in uniaxial compression of the Si sample (along the $\langle 110 \rangle$ direction). We approximate the strain and stress very roughly to be 2000 ppm and 0.34 GPa, respectively (error estimates are $\approx \pm 500$ ppm and ≈ 0.09 GPa for the strain and stress, respectively).

The muon spin polarization was studied using the longitudinal (LF) μSR technique[1] where the applied external field **H** is applied parallel to a $\langle 100 \rangle$ direction of the Si sample, as well as the the initial muon spin direction. Due to the highly anisotropic hyperfine interaction of Mu_{BC}^0, and in a sufficiently high applied field **H**, half the muons can be visualized[1,15,16] as precessing about an effective field corresponding to the electron quantum number $m_s = +1/2$ while the other half precesses about an effective field corresponding to $m_s = -1/2$. (The two precession frequencies are usually labeled as ν_{12} and ν_{34} in the literature.) In general, these effective fields differ from **H** in both magnitude and direction.[1,15] As a consequence, although the initial muon spin is parallel to **H**, a precessing signal(s) of significant magnitude can be observed at certain applied magnetic fields. Of particular interest in our experiment is the existence of a so-called "magic field" of magnitude H_{mag} where the precession frequency ν_{mag} is essentially independent of the angle θ between **H** and the Mu_{BC}^0 hyperfine symmetry axis[13] (also the bond axis). The analytical approximations for H_{mag} and ν_{mag} are given by

$$H_{mag} = \left| \frac{A_{\parallel} + A_{\perp}}{4\tilde{\gamma}_{\mu}} \right| \tag{1}$$

and

$$\nu_{mag} = \left| \frac{A_{\parallel} - A_{\perp}}{4} \right|, \tag{2}$$

where $\tilde{\gamma}_{\mu} = 13.554$ MHz/kG. In the case of unstressed silicon, and using the known hyperfine parameters for Mu_{BC}^0, these equations give $H_{mag} = 2.02$ kG and $\nu_{mag} = 18.94$ MHz. (A more accurate numerical calculation gives $H_{mag} = 2.002$ kG and $\nu_{mag} = 19.10$ MHz.) The advantage of carrying out measurements at (or close to) H_{mag} is that since the precession frequency does not depend on the orientation between the crystal and the magnetic field, a long lived precession signal is expected in the absence of any dynamics. In other words, the four $\langle 111 \rangle$ bond directions all give the same frequency if their hyperfine constants are equal (this is the case in an unstressed sample), and the exact orientation of the sample relative to the external field is unimportant. Hence, any significant changes of the muon spin polarization under stress can be attributed to changes in the hyperfine parameters due to the applied stress.

Initially, measurements were carried out in the absence of stress. The experiments were performed at 17.5 K with an applied field **H** of 2.02 kG [as estimated from the value of the precession frequency shown in Fig. 1(a)], close to the magic field, applied parallel to one of the $\langle 100 \rangle$ directions (i.e., the face) of the crystal as well as the initial muon polarization. In this configuration, the Mu_{BC}^0 centers are all equivalent with $\theta = 54.7°$. Figure 1(a) shows the asymmetry plot, and Fig. 2(a) its Fourier transform, in the absence of stress. As shown in Fig. 1(a), the data are well fitted in the time domain to a single Gaussian damped precession signal. Note that as expected, the fitted frequency of 19.001(3) MHz is close to the "magic frequency" discussed above. Furthermore, the spectrum shows very little relaxation. This is not surprising since in undoped Si samples at these temperatures, Mu_{BC}^0 is stable (on the lifetime of the muon), there are very few free charged carriers, and hence so-called charge and/or spin exchange interactions are negligible.[23,24]

The spectrum is dramatically changed when uniaxial compressional stress is applied along one of the $\langle 110 \rangle$ directions (and perpendicular to **H**). This is shown in Figs. 1(b)

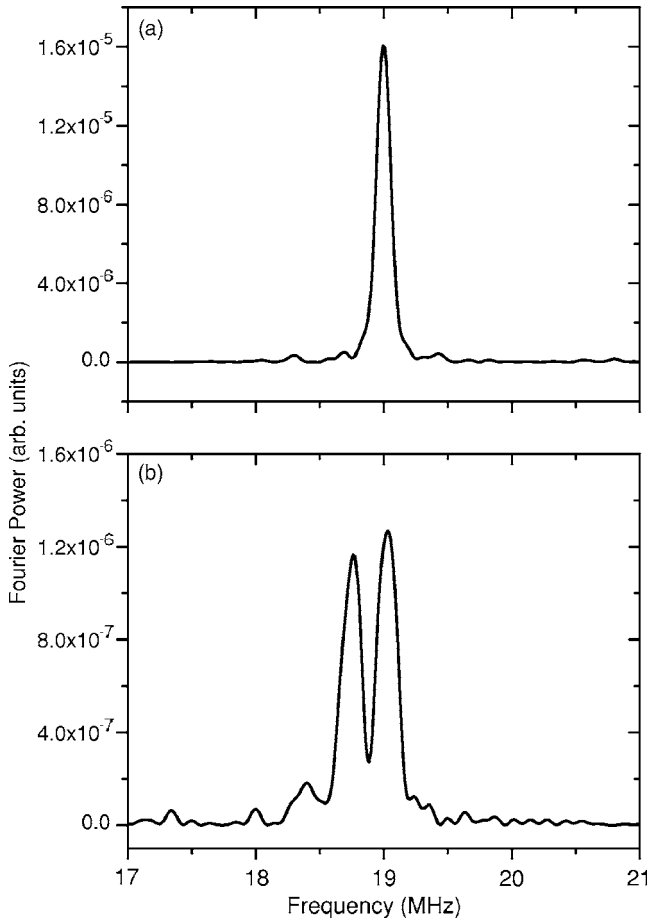

FIG. 2. Fourier transforms of the data displayed in Fig. 1, i.e., (a) in the absence of any applied stress and (b) with the application of uniaxial compressive stress.

and 2(b). As indicated in Fig. 1(b), the time-domain spectrum is well fitted to a sum of two Gaussian damped precession signals. One frequency is at 18.992(5) MHz, very similar to that measured in the original unstressed sample, while the second frequency is at 18.788(7) MHz.[25] Note that after these measurements, the unstressed Si sample is studied again. A single frequency at 19.001(2) MHz is observed, i.e., the same as initially. This implies that no permanent local deformation of the sample has taken place.

The observation that the unstressed line splits into two upon the application of a uniaxial compressive stress is expected, given the direction of the applied stress with respect to the crystalline axes of silicon. Since the stress is applied along a $\langle 110 \rangle$ direction, and Mu_{BC}^{0} resides in a Si-Si bond, half of the Mu_{BC}^{0} centers are at $\phi = 35.3°$ while the other half are at $\phi = 90°$. The symbol ϕ designates the angle between the principal axis of the hyperfine tensor (i.e., Si-Si bond direction) and the direction of the stress field.

Given that we have applied a stress of -2000 ppm along the $\langle 110 \rangle$ direction, we can use the tabulated elastic constants of silicon[26] to calculate that the $\langle 111 \rangle$ lattice vectors along which the Si-Si bonds lie should change by -1092 and $+326$ ppm for $\phi = 35.3°$ and $\phi = 90°$, respectively. The breaking of the crystal symmetry by the strain allows the two Si sublattices to move relative to each other along $\langle 001 \rangle$, allowing the bond lengths to remain nearer to equal to each other. This effect is described by the internal strain parameter ζ. Using the experimental value for silicon of $\zeta = 0.73 \pm 0.04$ (Refs. 27 and 28) we obtain bond length changes of -575 and -192 ppm—although both bond lengths now decrease, the $\phi = 35.3°$ bond still undergoes the larger strain. Therefore, we assign the lower frequency signal in Fig. 2(b), which has changed most from the unstrained measurement, to the $\phi = 35.3°$ centers and the upper frequency signal to the $\phi = 90°$ centers. Note that the observed frequencies, when compared to the unstressed signal, do not change in the 3:1 ratio predicted above. This could indicate that either the elasticity of the Si-Mu_{BC}-Si bond is different from the Si-Si bond and/or the hyperfine constants are not functions of the bond length alone.

For both sites, the applied stress breaks the initial D_{3d} threefold symmetry about the bond axis to C_{2h}, so we could expect the axial symmetry of the hyperfine constants to be broken. The bond direction can also rotate, as local distortions around the bond are permitted in addition to the bulk rotation of the $\langle 111 \rangle$ lattice vector towards $\langle 001 \rangle$. Therefore we now have, for each site, four parameters that will determine the value of the observed frequency: the new θ, and the three principal hyperfine constants A_1 (formerly $A_\parallel$) at θ to $\langle 001 \rangle$, A_2 (formerly $A_\perp$) at $90° + \theta$ in the plane containing the bond and $\langle 001 \rangle$ directions, and A_3 (formerly $A_\perp$) perpendicular to that plane.

Note that the bonds at $\phi = 90°$ rotate differently than the ones at $\phi = 35.3°$ since the Poisson's ratios $\epsilon_{\langle 1\bar{1}0 \rangle} / \epsilon_{\langle 110 \rangle}$ and $\epsilon_{\langle 001 \rangle} / \epsilon_{\langle 110 \rangle}$ are not equal and the sample expands much more along $\langle 001 \rangle$.

The changes in frequency at constant field close to $\mathbf{H}_{mag} \| \langle 001 \rangle$ can be calculated (and confirmed by simulations) as

$$\frac{\partial |\nu|}{\partial A_1} = \frac{\cos^2 \theta}{2} = +\frac{1}{6}, \tag{3}$$

$$\frac{\partial |\nu|}{\partial A_2} = -\frac{\sin^2 \theta}{2} = -\frac{1}{3}, \tag{4}$$

$$\frac{\partial |\nu|}{\partial A_3} = 0. \tag{5}$$

The measurements indicate that we have observed a change, compared to the unstressed values, of $(\Delta A_1 - 2\Delta A_2) = -1.28 \pm 0.05$ MHz for one site (probably $\phi = 35.3°$) and -0.054 ± 0.036 MHz for the other. The value of $(2\Delta A_1 + \Delta A_2)$ remains unknown as do $\Delta\theta$ and ΔA_3.

There is insufficient information in our current measurements to establish which hyperfine constants are changing. Hence, we are unable to ascertain whether the pressure dependence is due to the change of the contact interaction, the change of axial-dipolar interaction, or even the appearance of a nonaxial dipolar term in the hyperfine interaction. Such information can potentially be obtained by carrying out analagous measurements at different applied fields and field orientations, which are being planned.

In summary, we have demonstrated that uniaxial compressive stress can produce significant changes in the electronic structure of Mu^0_{BC}. The redistribution of the unpaired spin density in the vicinity of the muon modifies the hyperfine parameters of Mu^0_{BC} and produces easily noticeable changes of its precession signatures.

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[1] K. H. Chow, B. Hitti, and R. F. Kiefl, in *Identification of Defects in Semiconductors*, Semiconductors and Semimetals Vol. 51A, edited by M. Stavola (Academic Press, New York, 1998), p. 137.
[2] S. F. J. Cox, J. Phys.: Condens. Matter **15**, R1727 (2003).
[3] 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).
[4] K. H. Chow, B. Hitti, R. F. Kiefl, S. R. Dunsiger, R. L. Lichti, and T. L. Estle, Phys. Rev. Lett. **76**, 3790 (1996).
[5] R. Kadono, A. Matsushita, K. Nagamine, K. Nishiyama, K. H. Chow, R. F. Kiefl, A. MacFarlane, D. Schumann, S. Fujii, and S. Tanigawa, Phys. Rev. B **50**, 1999 (1994).
[6] K. H. Chow, B. Hitti, R. F. Kiefl, R. L. Lichti, and T. L. Estle, Phys. Rev. Lett. **87**, 216403 (2001).
[7] B. E. Schultz, K. H. Chow, B. Hitti, Z. Salman, S. R. Kreitzman, R. F. Kiefl, and R. L. Lichti, Phys. Rev. B **72**, 033201 (2005).
[8] B. E. Schultz, K. H. Chow, B. Hitti, R. F. Kiefl, R. L. Lichti, and S. F. J. Cox, Phys. Rev. Lett. **95**, 086404 (2005).
[9] R. L. Lichti, S. F. J. Cox, K. H. Chow, E. A. Davis, T. L. Estle, B. Hitti, E. Mytilineou, and C. Schwab, Phys. Rev. B **60**, 1734 (1999).
[10] K. Shimomura, R. Kadono, K. Ohishi, M. Mizuta, M. Saito, K. H. Chow, B. Hitti, and R. L. Lichti, Phys. Rev. Lett. **92**, 135505 (2004).
[11] R. L. Lichti, W. A. Nussbaum, and K. H. Chow, Phys. Rev. B **70**, 165204 (2004).
[12] R. C. Vilao, H. V. Alberto, J. P. Duarte, J. M. Gil, A. Weidinger, N. Ayres de Campos, R. L. Lichti, K. H. Chow, and S. F. J. Cox, Phys. Rev. B **72**, 235203 (2005).
[13] B. D. Patterson, Rev. Mod. Phys. **60**, 69 (1988).
[14] R. F. Kiefl and T. L. Estle, in *Hydrogen in Semiconductors*, Semiconductors and Semimetals Vol. 34, edited by J. Pankove, N. M. Johnson (Academic Press, New York, 1990), p. 547.
[15] R. F. Kiefl, M. Celio, T. L. Estle, S. R. Kreitzman, G. M. Luke, T. M. Riseman, and E. J. Ansaldo, Phys. Rev. Lett. **60**, 224 (1988).
[16] K. H. Chow, R. F. Kiefl, B. Hitti, T. L. Estle, and R. L. Lichti, Phys. Rev. Lett. **84**, 2251 (2000).
[17] E. Holzschuh, Phys. Rev. B **27**, 102 (1983).
[18] C. Kittel, *Introduction to Solid State Physics*, 8th ed. (Wiley, New York, 2004), p. 52.
[19] C. G. Van de Walle, in *Hydrogen in Semiconductors*, Semiconductors and Semimetals vol. 34, edited by J. Pankove, N. M. Johnson (Academic Press, New York, 1990), p. 585.
[20] K. W. Blazey, J. A. Brown, D. W. Cooke, S. A. Dodds, T. L. Estle, R. H. Heffner, M. Leon, and D. A. Vanderwater, Phys. Rev. B **23**, 5316 (1981).
[21] K. W. Blazey, T. L. Estle, E. Holzschuh, W. Odermatt, and B. D. Patterson, Phys. Rev. B **27**, 15 (1983).
[22] K. G. Lyon, G. L. Salinger, C. A. Swenson, and G. K. White, J. Appl. Phys. **48**, 865 (1977).
[23] K. H. Chow, R. F. Kiefl, J. W. Schneider, B. Hitti, T. L. Estle, R. L. Lichti, C. Schwab, R. C. DuVarney, S. R. Kreitzman, W. A. MacFarlane, and M. Senba, Phys. Rev. B **47**, 16004 (1993).
[24] K. H. Chow, R. L. Lichti, R. F. Kiefl, S. Dunsiger, T. L. Estle, B. Hitti, R. Kadono, W. A. MacFarlane, J. W. Schneider, D. Schumann, and M. Shelley, Phys. Rev. B **50**, 8918 (1994).
[25] We have also carried out measurements using several different snug fits, i.e., less pieces of aluminum foil, between the sample and the copper holder. As the stress is increased, the line shown in Fig. 2(a) initially broadens and eventually evolves into the doublet that is seen in Fig. 2(b). A more careful quantitative measurement of this effect would be interesting, but has not been carried out yet.
[26] J. J. Wortman and R. A. Evans, J. Appl. Phys. **36**, 153 (1965).
[27] H. D'Amour, W. Denner, H. Schulz, and M. Cardona, J. Appl. Crystallogr. **15**, 148 (1982).
[28] C. S. G. Cousins, L. Gerward, J. Staun Olsen, B. Selsmark, and B. J. Sheldon, J. Appl. Crystallogr. **15**, 154 (1982).