Bond-Centered Hydrogen or Muonium in Diamond: The Explanation for Anomalous Muonium and an Example of Metastability

T. L. Estle
Physics Department, Rice University, Houston, Texas 77251

S. Estreicher
Physics Department, Texas Tech University, Lubbock, Texas 79409

and

D. S. Marynick
Department of Chemistry, University of Texas at Arlington, Arlington, Texas 76019

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We present quatitative theoretical evidence that interstitial bond-centered hydrogen or muonium in diamond is stable as a result of unusually large lattice relaxation. The two geometrical configurations of neutral interstitial muonium explain the structures and properties of anomalous muonium (bond centered) and normal muonium (tetrahedral interstitial site), including the thermal conversion of normal to anomalous muonium, and represent a well-defined example of interstitial metastability.

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Isolated atomic hydrogen has never been observed by electron spin resonance (ESR) in any semiconductor, presumably because the formation of H_2 molecules or associates of hydrogen with other defects are too probable at concentrations large enough to do ESR experiments. Yet a great deal is known experimentally about a pseudoisotope of hydrogen, muonium, where the proton is replaced by a positive muon (μ^+). Muonium, which is radioactive, is otherwise similar to hydrogen in its physical properties, except for those which depend on the mass ($m_p \approx 9m_\mu$). Two quite different muonium-defect centers are observed in diamond,[1] Si,[2,3] Ge,[4] GaP,[5] and GaAs.[5] The normal-muonium (Mu) hyperfine interaction is isotropic and, in group IV and III-V semiconductors, its value ranges from 0.45 (in Si[2,3]) to 0.83 (in diamond[1]) of the free-muonium value. Thus, the wave function of Mu has a significant amount of atomic 1*s* character but is somewhat delocalized. Recent theoretical calculations[6-8] confirm that the equilibrium site of Mu in diamond is the tetrahedral interstitial site. In Si and Ge, there is experimental evidence that Mu is rapidly diffusing.[9-11] The other observed muonium-defect center, anomalous muonium (Mu*), has quite different properties. In all five crystals in which Mu* has been seen, the hyperfine interaction has trigonal symmetry and its average value as a fraction of the free-muonium value ranges from 0.015 (in Si[3]) to 0.046 (in diamond[1]). Further, in diamond the experimental data between 350 and 800 K demonstrate that Mu is thermally converting to Mu*, and above 800 K only Mu* is present.[1,12,13]

Although the muon spin-rotation spectra of Mu* were first seen over thirteen years ago,[2] no satisfactory explanation for the structure of this defect was published until Symons and Cox[14,15] proposed, using chemical-bonding arguments, that Mu* is a bond-centered interstitial. Were this conjecture correct, Mu and Mu* would be an example of defect metastability (coexistence of two distinct atomic arrangements for a single charge state of a defect). In recent years there has been extensive research on bistability and metastability[16] of defects with such notable examples as the *EL*2 center in GaAs,[16] the *M* center in InP,[17] and In-doped CdF_2.[18] In the present case, the signatures of Mu and Mu* are their muon spin-rotation spectra which provide information comparable to ESR. Hence a considerable amount of experimental information exists on both configurations.[1,3,4]

We present here calculations[19] which demonstrate that the bond-centered site for interstitial muonium (or hydrogen) is significantly more stable than the tetrahedral interstitial site because of the large lattice relaxation for the former. The properties of the bond-centered interstitial are consistent with all experimental data on anomalous muonium in diamond and the combined experimental and theoretical information strongly supports the view that Mu and Mu* are different geometrical configurations of neutral interstitial muonium.

Most of our calculations were done at the Hartree-Fock (HF) level with the use of the approximate *ab initio* method of partial retention of diatomic differential overlap[20-22] (PRDDO) which accurately reproduces minimal-basis-set *ab initio* HF calculations at a fraction of the cost (see Refs. 7, 8, and 20–22). We simulate the host crystal using ten different clusters containing up to 87 atoms and centered at the tetrahedral (*T*), hexagonal (*H*), or bond-centered (BC) interstitial sites, or at substitutional site. For diamond, the C—C bond length is set equal to 1.545 Å before relaxation[8] and the dangling bonds are saturated by hydrogen atoms with a C—H bond length of 1.09 Å.[7,8,23] With this C—H bond length, the properties of the defect (energy differences, spin distribution, equilibrium geometry, etc.) converge rapidly with increasing cluster size and become independent of its center. Except as noted, we report below the results obtained with $C_{44}H_{42}Mu$, which is centered at the BC site and is complete through the closest five shells around its center. In this cluster the second nearest neighbors (nn) to the BC site are not directly connected to the hydrogen saturators and therefore can also be relaxed. Finally, this cluster contains both T and H sites with complete first- and second-nn shells.

When the muon is at the T site, there is a small outward relaxation of the first and second nn and the T site is a minimum of the total energy.[8] For the clusters used in Ref. 8, the total energy with Mu at the relaxed T site is 7.4 eV above that of the cluster at equilibrium with Mu at infinity. The unrelaxed BC site is a saddle point 13.9 eV above the relaxed T site. However, if the muon is at the BC site and the two nn are relaxed along the direction of the bond, the total energy drops by 15.9 eV as the C—C bond length increases by 42%! The relaxation of the second nn causes an additional lowering of the total energy by 0.7 eV. We did not consider the effects of relaxation of further shells. Thus, in the equilibrium configuration, the BC site is 2.7 eV *below* the relaxed T site (see Fig. 1). The C-Mu separation in the C—Mu —C bond is 1.10 Å (very close to the equilibrium C—H bond length in, e.g., CH_4), the C—C bond length between first and second nn to the BC site is 1.497 Å, and that between second and third nn is 1.550 Å. The second-first-second-nn bond angle is 117.5° and the muon-first-second-nn bond angle is 99.1° (in the perfect crystal, these values are 1.545 Å and 109.5°). No tendency of the muon or of its two nn to move off the bond axis is apparent in our calculations nor is there any evidence of an asymmetric positioning of the muon resembling any of the interstitialcies which have been reported for other impurities in silicon.[24] Although the displacements of the nn atoms are large, the differences in the bond lengths relative to those in the perfect crystal are smaller than the relative differences in the bond angles. This is consistent with the behavior expected of covalent systems.

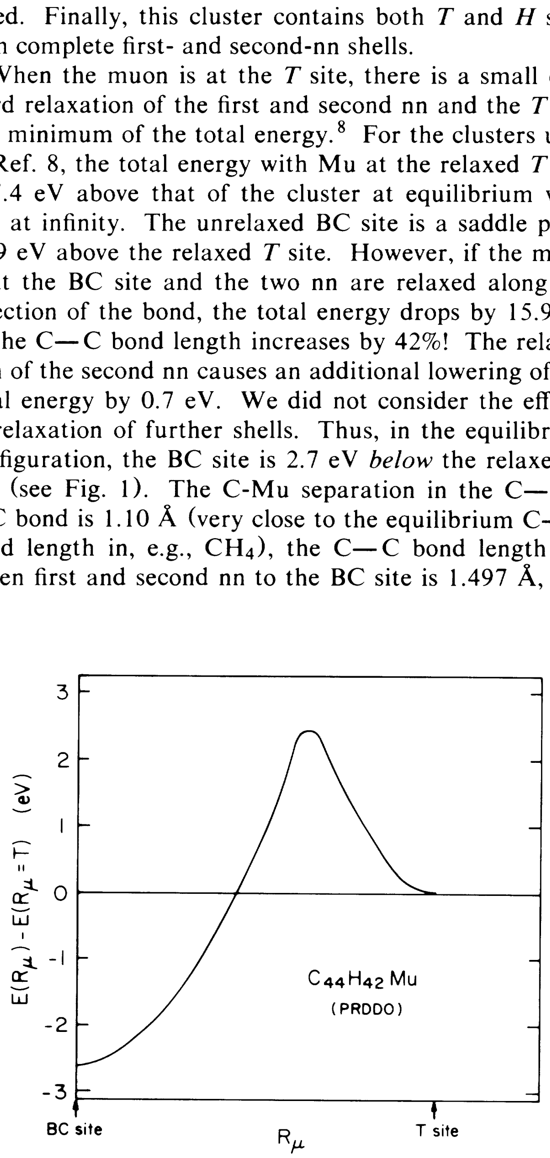

FIG. 1. Potential barrier for a muon or hydrogen atom between a fully relaxed bond-centered site and a fully relaxed tetrahedral interstitial site. The positions of the atoms for intermediate values of R_μ were obtained by linear interpolation of their coordinates.

In the $C_{20}H_{32}Mu$ cluster, which is centered at the H site, the curvature of the total energy is about 5 times larger for displacements of the muon along the bond than along directions perpendicular to it, implying that the muon vibrates predominantly in the nodal plane. Linear interpolations between the relaxed T (H) site and the relaxed BC site were used to estimate the upper limit to the barrier height between them. A value of 2.4 eV (2.1 eV) above the relaxed T (H) site was found. The saddle point occurs for the muon about 66% (79%) of the BC-to-T (BC-to-H) distance away from the BC site. The figure shows the potential barrier for a muon between a relaxed BC site and a relaxed T site. The curve is the total energy between the end points calculated by the use of coordinates interpolated linearly between their relaxed BC and T values (i.e., the geometry was optimized only at the BC and T sites). Since expanded-basis-set calculations usually result in lower potential barriers (see, e.g., Ref. 8), since the saddle point may not lie on the interpolated path, and since the zero-point energy of a muon at the T site is rather large,[7,8] we expect the height of the BC-T potential barrier to be significantly lower than the values deduced from the figure. This suggests a T-to-BC transition above room temperature and provides a straightforward explanation for the Mu-to-Mu* transition in diamond.[1,12,13]

If the muon is at the T site, the reduced hyperfine parameter (ratio of the contact interaction to that of free muonium) at the HF level is larger[8] than the one observed[1] (about 1.30 vs 0.83). This is true for PRDDO as well as *ab initio* HF irrespective of the basis set used.[8] If the muon is at the BC site, the reduced hyperfine constant calculated by PRDDO is −0.19. The experimental[1,13] value for Mu* is −0.05. While the signs agree, the magnitude is off by a factor of 4. However, the absolute error is remarkably small, about 14% of the atomic value. We investigated basis-set effects using a much smaller cluster, C_2H_6Mu, and found the following reduced hyperfine parameters: −0.16 (PRDDO), −0.19 (*ab initio*, minimal basis set), −0.22 (*ab initio*, double-zeta basis set), and −0.21 (*ab initio*, polarized double zeta). In all cases, most of the positive spin density is on the first nn to the muon. This indicates that the dipolar hyperfine constant is positive. The qualitative agreement with the observed properties of Mu* is obvious.[1]

While an accurate calculation of the spin density would require a rather large configuration-interaction (CI) wave function, the qualitative effects of correlation can be examined by limited CI expansions. A small CI calculation with a 4-31G basis set on C_2H_6Mu was carried out for this reason. The number of configurations was restricted by our (a) starting with a restricted open-shell HF wave function and localizing the doubly occupied orbitals, (b) exciting only the electrons in the localized C-Mu-C orbital and the singly occupied orbital, and (c) restricting the virtual space to nondegenerate orbitals. These restrictions have the effect of adding electron correlation mainly in the C-Mu-C region. The calculation results in a wave function with 242 configurations, but only two of the configurations have coefficients larger than 0.05 and both correspond to single excitations of the odd electron into unoccupied orbitals with a large excess of positive spin density on the muon. Because the orbitals involved are similar in the unrestricted and restricted open-shell HF calculations, we expect that CI corrections to the unrestricted-HF spin density will render the contact density on the muon less negative, i.e., closer to the experimental value.

The electronic structure of muonium at the BC site has been discussed qualitatively by Cox and Symons.[15] We would like to add to their discussion that three-center bonding interactions are common in structural chemistry. Many boron compounds exist in which hydrogens are bonded to two borons, e.g., the doubly bridged compound diborane.[25] While bridging hydrogens between carbons are rare in stable organic compounds, they are well established as intermediates in organic reactions and as stable cations in some solvents.[26]

In summary, hydrogen or muonium forms a very stable bond-centered interstitial in diamond. The properties of bond-centered muonium are such a good match with those of anomalous muonium that there is little doubt that anomalous muonium is neutral muonium at the center of a covalent bond in diamond. Normal muonium has been associated with neutral muonium at the tetrahedral interstitial site, which is a local minimum of the total energy.[7,8] Thus neutral interstitial muonium (or hydrogen) exists with two distinct geometrical configurations, one at the BC site (stable) and one at the T site (metastable). The thermal conversion of the metastable to the stable configuration is the transition from Mu to Mu* seen near 700 K in diamond. The tetrahedral interstitial is metastable because the large lattice relaxation of the bond-centered interstitial makes tunneling improbable, and because the moderate energy barrier between the two prevents thermal conversion at low temperatures. Preliminary calculations of bond-centered muonium in Si show that a relaxation of about 35% makes the BC site more stable than the T site. However, in the metastable configuration, the muon diffuses rapidly at low temperatures in Si.[9]

Finally, one might ask whether a change in the charge of the impurity would result in a change in the local geometry of the defect, i.e., in a bistable[16] interstitial. Perhaps the changes in the muon channeling from π^+ decay in germanium and gallium arsenide[27] when the samples are illuminated with light are examples of bistability in the analogous pionium-defect system. Unfortunately the authors of that study did not examine the bond-centered site as a possible site for the pion. The qualitative channeling behavior would differ little from that for the hexagonal site, which they did consider.

It has come to our attention that a pertinent paper appeared[28] about the time that our paper was finished. That paper described a minimal-basis-set unrestricted-HF calculation on a $C_{10}H_{16}$ cluster. Their results provided quantitative support for the qualitative arguments presented in Refs. 14 and 15. However, all of the BC sites for the $C_{10}H_{16}$ cluster are at the surface of the cluster and the nn host atoms of the muon are bonded to either one of two hydrogen saturators. Since these nn atoms are displaced appreciably in the relaxation, the smallness of the cluster used would appear to be a severe limitation. In fact we find only small quantitative differences between our results and those reported in Ref. 28.

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[1] E. Holzschuh, W. Kündig, P. F. Meier, B. D. Patterson, J. P. F. Sellschop, M. C. Stemmet, and H. Appel, Phys. Rev. A **25**, 1272 (1982).

[2] J. H. Brewer, K. M. Crowe, F. N. Gygax, R. F. Johnson, B. D. Patterson, D. G. Fleming, and A. Schenck, Phys. Rev. Lett. **31**, 143 (1973).

[3] B. D. Patterson, A. Hintermann, W. Kündig, P. F. Meier, F. Waldner, H. Graf, E. Recknagel, A. Weidinger, and Th. Wichert, Phys. Rev. Lett. **40**, 1347 (1978).

[4] E. Holzschuh, H. Graf, E. Recknagel, A. Weidinger, Th. Wichert, and P. F. Meier, Phys. Rev. B **20**, 4391 (1979).

[5] R. F. Kiefl, J. W. Schneider, H. Keller, W. Kündig, W. Odermatt, B. D. Patterson, K. W. Blazey, T. L. Estle, and S. L. Rudaz, Phys. Rev. B **32**, 530 (1985).

[6] N. Sahoo, S. K. Mishra, A. Coker, T. P. Das, C. K. Mitra, L. C. Snyder, and A. Glodeanu, Phys. Rev. Lett. **50**, 913 (1983).

[7] S. Estreicher, A. K. Ray, J. L. Fry, and D. S. Marynick, Phys. Rev. Lett. **55**, 1976 (1985).

[8] S. Estreicher, A. K. Ray, J. L. Fry, and D. S. Marynick, Phys. Rev. B **34**, 6071 (1986).

[9] B. D. Patterson, E. Holzschuh, R. F. Kiefl, K. W. Blazey, and T. L. Estle, Hyperfine Interact. **17–19**, 599 (1984).

[10] K. P. Döring, K. P. Arnold, M. Gladisch, N. Haas, E. E. Haller, D. Herlach, W. Jacobs, M. Krause, M. Krauth, H. Orth, and A. Seeger, Hyperfine Interact. **17–19**, 629 (1984).

[11] C. W. Clawson, K. M. Crowe, E. E. Haller, S. S. Rosenblum and J. H. Brewer, Hyperfine Interact. **17–19**, 603 (1984).

[12] B. D. Patterson, E. Holzschuh, W. Kündig, P. F. Meier, W. Odermatt, J. P. F. Sellschop, and M. C. Stemmet, Hyperfine Interact. **17–19**, 605 (1984).

[13] W. Odermatt, Hp. Baumeler, H. Keller, W. Kündig, B. D. Patterson, J. W. Schneider, J. P. F. Sellschop, M. C. Stemmet, S. Connell, and D. P. Spencer, Hyperfine Interact. **32**, 583 (1986).

[14] M. C. R. Symons, Hyperfine Interact. **17–19**, 771 (1984).

[15] S. F. J. Cox and M. C. R. Symons, Chem. Phys. Lett. **126**, 516 (1986).

[16] G. A. Baraff and M. Schlüter, Phys. Rev. Lett. **55**, 2340 (1985).

[17] M. Stavola, M. Levinson, J. L. Benton, and L. C. Kimerling, Phys. Rev. B **30**, 832 (1984).

[18] J. E. Dmochowski, J. M. Langer, and Z. Kalinski, Phys. Rev. Lett. **56**, 1735 (1986).

[19] Preliminary calculations were presented by T. L. Estle, S. Estreicher, and D. S. Maynick, Hyperfine Interact. **32**, 637 (1986).

[20] T. D. Halgren and W. N. Lipscomb, J. Chem. Phys. **58**, 1569 (1973).

[21] D. S. Marynick and W. N. Lipscomb, Proc. Nat. Acad. Sci. U.S.A. **79**, 1341 (1982).

[22] L. Throckmorton and D. S. Marynick, J. Comp. Chem. **6**, 652 (1985).

[23] N. Sahoo, K. C. Mishra, and T. P. Das, Phys. Rev. Lett. **57**, 3300 (1986); S. Estreicher, A. K. Ray, J. L. Fry, and D. S. Marynick, Phys. Rev. Lett. **57**, 3301 (1986).

[24] G. D. Watkins, in *Festkörperprobleme: Advances in Solid State Physics,* edited by P. Grosse (Vieweg, Braunschweig, 1984), Vol. 24, p. 163.

[25] L. S. Bartell and B. L. Carroll, J. Chem. Phys. **42**, 1135 (1965).

[26] R. P. Kirchen, N. Okazawa, K. Ranganayakulu, A. Rauk, and T. S. Sorensen, J. Am. Chem. Soc. **103**, 597 (1981).

[27] G. Flik, J. N. Bradbury, D. W. Cooke, R. H. Heffner, M. Leon, M. A. Paciotti, M. E. Schillaci, K. Maier, H. Rempp, J. J. Reidy, C. Boekema, and H. Daniel, Phys. Rev. Lett. **57**, 563 (1986).

[28] T. A. Claxton, A. Evans, and M. C. R. Symons, J. Chem. Soc., Faraday Trans. 2 **82**, 2031 (1986).