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Structure of negatively charged muonium in *n*-type GaAs

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Muon level-crossing resonance and muon-spin-rotation measurements on heavily doped *n*-type GaAs:Si and GaAs:Te show that the majority of positive muons implanted at room temperature form an isolated diamagnetic muonium center located at a high-symmetry site with Ga neighbors along the ⟨111⟩ direction(s). These experiments, together with theoretical considerations, imply that negatively charged muonium is at or near the tetrahedral interstitial site with four Ga nearest-neighbor atoms. Except for zero-point energy differences, these results should model negatively charged isolated hydrogen in GaAs.

Hydrogen is often an inadvertent impurity in elemental and compound semiconductors; it can modify the electrical activity of deliberate dopants and other defects or can itself act as a deep-level donor or acceptor. In the last decade, considerable experimental and theoretical work has led to an accurate microscopic description of many hydrogen defect centers including isolated atomic hydrogen.[1] The equilibrium charge state, the location, and the diffusivity of atomic hydrogen are expected to depend on the Fermi level. In heavily doped *n*-type semiconductors with the Fermi level close to the conduction band edge the negative charge state, H^-, should be favored, whereas in *p*-type semiconductors it would be the positive center, H^+. For *p*-type Si, theoretical calculations predict that H^+ located at the bond-centered (BC) site is the stable center, while for *n*-type material, the stable center is H^- at the tetrahedral interstitial (T) site.[2] In *n*-type GaAs, H^- is predicted to be stable near the T site with Ga nearest neighbors (T_{Ga}).[3–5] So far there is no direct experimental information on the structure of isolated H^- or H^+ in any semiconductor. The *presence* of H^- in *n*-type GaAs has been inferred from reverse-bias annealing experiments;[6] however, alternative explanations for these data have been proposed.[7]

Our knowledge of neutral atomic hydrogen in semiconductors is based primarily on studies of muonium [$Mu=\mu^+e^-$], a light hydrogen pseudoisotope with a positive muon replacing the proton.[8] The techniques of muon spin rotation (μSR) and muon level-crossing resonance (μLCR) have provided detailed information on the local electronic structure of *paramagnetic* Mu centers.[9–11] A *diamagnetic* μSR signal is also observed, corresponding to a center or centers with no unpaired electron spins. However, the lack of a hyperfine interaction makes this signal difficult to assign. Possible candidates include the singly charged ionic states, either Mu^- or Mu^+, and any diamagnetic complex containing Mu.

This paper concerns the diamagnetic muonium center in *n*-type GaAs: we report a spectroscopic signature based on the dipolar and muon-induced quadrupolar interactions with neighboring nuclei. This work yields the experimental determination of the local structure of a charged isolated muonium center in a semiconductor and provides a model for the hydrogen counterpart. The room temperature data establish an interstitial site with Ga nearest neighbor(s) along the ⟨111⟩ axes. In combination with theory, this result strongly

supports a model where Mu^- is at or near the T_{Ga} site. The observed center is distinct from that seen in p-type samples and its isolated nature is demonstrated by nearly identical results for GaAs:Si and GaAs:Te.

Experiments were performed at four muon facilities: LAMPF, TRIUMF, ISIS, and PSI. In all cases the muon beams had a nominal momentum of 30 MeV/c (giving an implantation depth of a few tenths of a mm in our homogeneously doped samples) and a spin polarization of close to 100%. The measurements consisted of monitoring the evolution of polarization, on the μs time scale, by two standard methods: (i) the transverse-field technique of muon spin rotation (TF-μSR), which displays a precession damped according to the distribution of local fields at the muon site, and (ii) the longitudinal-field technique of μLCR, which displays a characteristic spectrum of neighboring quadrupolar interactions via resonant cross relaxation. The μLCR and TF-μSR results on n-type GaAs:Si were taken at LAMPF and TRIUMF, respectively. Three wafers of n-type GaAs:Si with (100), (110), and (111) faces obtained from Laser Diode Inc. and a second (100) GaAs:Si wafer from Hewlett Packard were examined. The samples were all cut from material grown by the liquid encapsulated Czochralski method and had Si concentrations in the range $2.5–5\times10^{18}$ cm^{-3}. A similar study on a single n-type GaAs:Te (100) wafer was made by μLCR at ISIS and by TF-μSR at PSI. This sample, from Hewlett Packard, had a Te concentration of 4.5×10^{18} cm^{-3}. Comparative measurements were performed on a (100) wafer of p-type GaAs:Zn (2.8×10^{19} cm^{-3}) from Laser Diode Inc.

The measured quantity in a μLCR experiment is the time-integrated muon spin polarization $\bar{P}$ along the applied magnetic field $\mathbf{B}$.[12] For a diamagnetic center such as Mu^- the relevant terms in the spin Hamiltonian are the Zeeman interactions of the muon and neighboring nuclear spins with $\mathbf{B}$, the magnetic dipolar coupling between the muon and nuclear spins, and the nuclear electric quadrupolar interaction. Dips in $\bar{P}$ appear at values of the magnetic field where resonant cross relaxation between the muon and neighboring nuclear spins occurs due to avoided level crossings in the combined energy levels. The positions of resonances associated with a particular nucleus i are determined by the nuclear electric quadrupole parameter (Q^i) and the angle θ_i between $\mathbf{B}$ and the muon-nucleus direction $\hat{z}_i$. The intensities and widths of the resonances are a function of the magnetic dipolar parameter (D^i) for the muon-nucleus interaction and the number of equivalent nuclei (n).

Figure 1(a) shows the μLCR spectrum recorded for GaAs:Si at room temperature with $\mathbf{B}$ parallel to a $\langle100\rangle$ crystallographic axis. Five resonances are present in the field range shown and no additional resonances were observed up to 120 mT. The four upper resonances may be assigned with certainty to gallium. Each isotope, ^{69}Ga and ^{71}Ga, has spin 3/2 and contributes a pair of lines. The relative positions and intensities of the two doublets define a unique value of the field gradient since they scale, respectively, with the quadrupole moments q_i and natural abundances of the two isotopes. The small number of lines and the structure of the doublets implies that the principal axis of the electric field gradient tensor is parallel to $\langle111\rangle$ at an angle $\theta=54.74°$ to the magnetic field. Assuming the gradient to be directed towards the

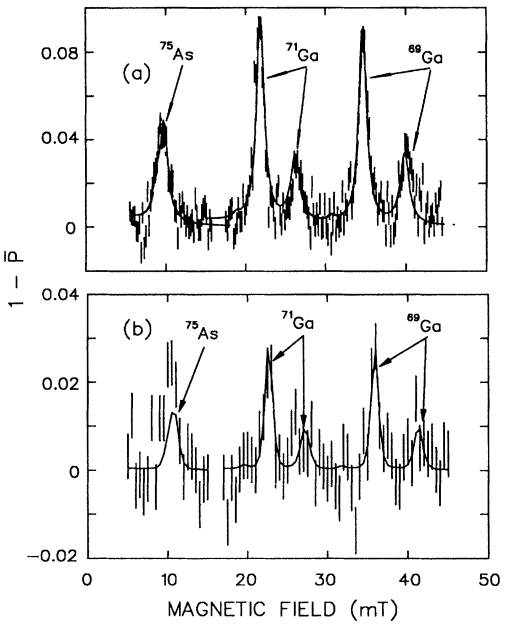

FIG. 1. Room temperature μLCR spectra for (a) GaAs:Si and (b) GaAs:Te. The data in (a) are for a full time integral, while those in (b) are for a delayed time window of 3 to 14 μs which enhances the amplitudes (Ref. 18). In (a), the fitted curves for the various site assumptions are virtually indistinguishable. The curve shown in (b) is for a T_{Ga} site assumption with the same values of D^i as in (a).

muon, this implies that the Ga neighbor(s) lie along $\langle111\rangle$ directions. The broader fifth resonance at lower field cannot be ascribed to gallium, since the isotopic signature is missing. It is therefore assigned to arsenic, for which the isotope ^{75}As, also with spin 3/2, is 100% abundant. The position of this resonance indicates a smaller field gradient at the As neighbors for which the structure in the resonance is not resolved.

There are three candidate sites compatible with these assignments,[13] namely, T_{Ga}, BC, and AB_{Ga} (antibonding to a Ga), all of which have a Ga along $\langle111\rangle$. It is not possible to determine n and D^i separately since the strength of a given resonance is determined by the product $\sqrt{n}D^i$. In particular, the spectrum does not in itself distinguish between the BC (one Ga neighbor) and T_{Ga} (four equivalent Ga neighbors) although the BC region can be excluded on theoretical grounds as explained below. Since on moving from T_{Ga} to AB_{Ga} only one of the Ga neighbors remains along $\langle111\rangle$, the AB_{Ga} site can only be compatible with the observed spectrum if the field gradient at the three further Ga neighbors is sufficiently small (not more than half that at the nearest As nuclei) to shift their resonances below 3 mT.

The fit quality and resulting nuclear quadrupole parameters Q^i for ^{69}Ga and ^{75}As (see Table I) were very similar for all three site assumptions. Although estimates of D^i and the corresponding distances r_i could be obtained from the μLCR intensities, more accurate values for the assumption of Mu^- in a T_{Ga} site were determined from conventional TF-μSR linewidth data. The frequency spectrum for Mu^- is the standard diamagnetic μSR signal consisting of a single

TABLE I. Fitted quadrupole parameters Q^i and the muon-nuclei distances for Mu^- at the T_{Ga} site in GaAs:Si and GaAs:Te. The r_{Ga} and r_{As} distances are 2.45 Å and 2.83 Å, respectively, for an undistorted T site.

	$\lvert Q(^{71}Ga)\rvert/h$ (MHz)[a]	$\lvert Q(^{75}As)\rvert/h$ (MHz)[a]	r_{Ga} (Å)	r_{As} (Å)
GaAs:Si	1.472(7)	0.636(9)	2.199(7)	2.72(5)
GaAs:Te	1.532(7)	0.70(1)	2.188(12)	2.82(14)

[a] $z(^{69}Ga)/q(^{71}Ga) = 0.178/0.112$. Errors are statistical.

line at the Larmor frequency of the muon. The linewidth was fitted using a Gaussian relaxation function [$\propto \exp(-\sigma^2 t^2)$]. The field dependence of σ may be theoretically calculated as first described by Hartmann.[14] Roughly speaking, when the nuclear Zeeman interaction is smaller than the nuclear quadrupolar interaction the latter controls the width and the nuclei are quantized along $\hat{z}_i$. In the opposite extreme the quantization axis is along **B** and σ reduces to the Van Vleck dipolar width, which vanishes for $3\cos^2\theta - 1 = 0$.

Figure 2(a) shows the field dependence of the measured width in GaAs:Si for the three primary crystallographic directions. The dramatic decrease in σ with increasing magnetic field when **B** is parallel to a $\langle 100 \rangle$ direction is strong confirmation that the muon and the nucleus dominating the dipolar interaction lie on the same $\langle 111 \rangle$ axis. The magnetic field at which this decrease occurs is a rough measure of the quadrupolar interaction for that nucleus. In fact, these data defined a search region for the resonances displayed in Fig. 1. Assuming the T_{Ga} site and the Q^i obtained from the μLCR data, D^i and hence r_i were obtained from a global fit of the TF-μSR linewidth data for the three orientations taking into account nearest neighbor Ga and next-nearest neighbor As nuclei. A second fit was performed with the additional constraint that D_{Ga}/D_{As} is fixed at the ratio obtained from the μLCR data. The results are given in Table I. The quoted errors on r_i reflect the small differences between the two types of fits, which primarily affect the next-nearest neighbor distances. Based on these T_{Ga} fits, we conclude that the effective Ga-muon distance is about 10% shorter than expected for an undistorted GaAs lattice. This could be largely attributed to the zero-point motion of the muon, whose light mass (about one-ninth that of the proton) implies a significant rms displacement from the classical equilibrium position, bringing it on average closer to its Ga neighbors than if it were located exactly at the T_{Ga} site. More interestingly, it may also indicate some contraction of the tetrahedral cage about the muon. Recent calculations[15] predict about 3% inward relaxation of Ga atoms toward a static H^- at the T_{Ga} position.

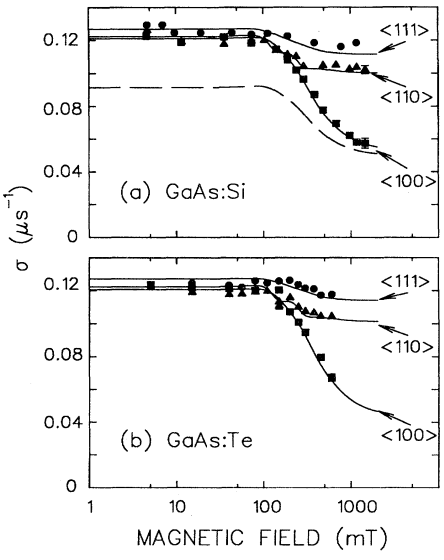

FIG. 2. The muon spin depolarization rate σ as a function of magnetic field in (a) GaAs:Si and (b) GaAs:Te. The solid curves are for a fit assuming a T_{Ga} muon site and allowing symmetric lattice distortions. The long-dashed curve in (a) is for **B** || $\langle 100 \rangle$ in an undistorted lattice.

Very similar results were obtained for n-type GaAs:Te. In particular, the *positions* of the resonances in the μLCR spectrum of Fig. 1(b) are very similar to that in Fig. 1(a). The relative intensities of the Ga and As lines appear to be different; this is probably a consequence of the lower statistics of the GaAs:Te data. The TF-μSR decoupling curves, shown in Fig. 2, are also very similar for the two samples. The Q^i's, which are insensitive to the site assumption, are obtained from the μLCR spectrum, then fixed in the fits to the TF-μSR data as described above.[16] The near equality of the values for the fitted parameters between GaAs:Si and GaAs:Te (see Table I) is strong evidence that the observed centers are not closely associated with a dopant atom, as for the muonium analog of the H-donor passivation complex. The Mu-Si and Mu-Te complexes would have different μLCR spectra since the Si donor substitutes at a Ga site whereas Te substitutes at an As site. Hence, we conclude that the observed center is effectively isolated.

We emphasize that the BC and AB_{Ga} sites are not excluded experimentally. Analyses for these sites yield distances of $r_{Ga} = 1.75(2)$ Å and $r_{As} = 1.95(3)$ Å for a BC site (a 51% Ga-As bond stretch) and $r_{Ga} = 1.75(2)$ Å and $r_{As} = 2.42(3)$ Å for an (undistorted) AB site where purely statistical errors are quoted. However, the electron-rich BC site is highly unlikely since this site is theoretically[3] the least stable (highest energy) location for Mu^-. Theory predicts that Mu^- is lowest in energy when occupying regions of low valence charge such as an interstitial T site. Calculations of the adiabatic potential energy surface[3,15] place the overall minimum off center from T_{Ga} but at only slightly lower energy with small barriers. The large muon zero-point energy then yields a state spread out over the entire tetrahedral cage, centered at T_{Ga}, and including all four AB_{Ga} sites.

The magnitude of the μLCR resonances and the static line broadening seen in TF-μSR imply that Mu^- is essentially confined to a single T_{Ga} cage on the time scale of the muon lifetime. This may seem surprising since Mu_T^0 diffuses rapidly at all temperatures on a μs time scale in high resistivity GaAs.[9] Several factors may be responsible for the small diffusion rate in the case of Mu^-. A significant lattice distortion (one interpretation of the results in Table I) would reduce the tunneling matrix element. Also, ionicity of GaAs lowers the energy for Mu^- in the T_{Ga} region due to Coulomb interactions and raises the energy of the T_{As} region.[15] Consequently, the energy barrier for Mu^- to hop to the next

equivalent site is larger and broader than for Mu_T^0. Since the equilibrium structure is relatively insensitive to isotopic mass, our Mu^- results should closely model isolated H^- in GaAs; although, the heavier H^- should be even less mobile.

Finally, our assertion that Mu^- is present in n-type material and Mu^+ forms in p-type material is consistent with the observation that the diamagnetic center observed in p-type GaAs:Zn is not the same as in the n-type samples: the μLCR spectrum is not seen up to 0.2 T, the diamagnetic μSR amplitude and linewidth have different temperature dependences, and the width shows a different field dependence in the p-type material.[17] These observations, along with the expected state change with Fermi level position, establish that the present data are for the isolated Mu^- center.

In conclusion, we have experimentally determined the nuclear quadrupole and muon-nuclear dipolar parameters for a charged diamagnetic muonium center in heavily doped n-type GaAs at room temperature. These results, along with theoretical arguments, experimental differences between n- and p-type samples, and the near equivalence for two n-type dopants indicate that the observed center is negatively charged muonium (Mu^-) located at or near a T_{Ga} site. This center does not undergo diffusive motion on the time scale of a few μs and is not paired with a donor atom.

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[1] *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, Berlin, 1992); Mater. Sci. Forum **148-149** (1994).

[2] C.G. Van de Walle *et al.*, Phys. Rev. B **39**, 10 791 (1989); Phys. Rev. Lett. **60**, 2761 (1988); K.J. Chang and D.J. Chadi, *ibid.* **60**, 1422 (1988); Phys. Rev. B **40**, 11 644 (1989).

[3] L. Pavesi and P. Giannozzi, Phys. Rev. B **46**, 4621 (1992).

[4] S.M. Myers *et al.*, Rev. Mod. Phys. **64**, 559 (1992).

[5] S.K. Estreicher, Mater. Sci. Forum **148-149**, 349 (1994).

[6] A.J. Tavendale *et al.*, Appl. Phys. Lett. **56**, 949 (1990); G. Roos *et al.*, *ibid.* **59**, 461 (1991); M.H. Yuan *et al.*, *ibid.* **58**, 925 (1991); A.W.R. Leitch *et al.*, Phys. Rev. B **44**, 1375 (1991).

[7] R.A. Morrow, J. Appl. Phys. **74**, 6174 (1993).

[8] B.D. Patterson, Rev. Mod. Phys. **60**, 69 (1988); R.F. Kiefl and T.L. Estle, in *Hydrogen in Semiconductors* (Ref. 2), p. 547.

[9] J.W. Schneider *et al.*, Mater. Sci. Forum **83-87**, 569 (1992); R. Kadono *et al.*, Hyperfine Interact. **64**, 635 (1990).

[10] R.F. Kiefl *et al.*, Phys. Rev. Lett. **58**, 1780 (1987).

[11] J.W. Schneider *et al.*, Phys. Rev. B **47**, 10 193 (1993).

[12] R.F. Kiefl and S.R. Kreitzman, in *Perspectives in Muon Science*, edited by T. Yamazaki, K. Nakai, and K. Nagamine (Elsevier, New York, 1992), p. 265; S.F.J. Cox, Z. Naturforsch. **47a**, 371 (1992).

[13] See Fig. 16 of Ref. 4 or Fig. 2 of Ref. 5.

[14] O. Hartmann, Phys. Rev. Lett. **39**, 832 (1977); M. Camani *et al.*, *ibid.* **39**, 836 (1977); O. Hartmann *et al.*, *ibid.* **44**, 337 (1980).

[15] T.R. Adams *et al.*, Philos. Mag. B (to be published).

[16] The ratio D_{Ga}/D_{As} is fixed to the GaAs:Si value.

[17] K.H. Chow *et al.*, Hyperfine Interact. **86**, 645 (1994).

[18] M. Leon, Phys. Rev. B **46**, 6603 (1992).