Determination of the Electronic Structure of Anomalous Muonium in GaAs from Nuclear Hyperfine Interactions

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Nuclear hyperfine structure of the anomalous muonium center (Mu*) in GaAs has been resolved in muon-spin-rotation frequency spectra and studied in detail by level-crossing-resonance spectroscopy. A comparison of the measured hyperfine parameters with the free-atom values indicates that 38% (45%) of the spin density is on one Ga (As) on the ⟨111⟩ symmetry axis of Mu* with the ratio of p to s spin density equal to about 4 (23). These results support a recently proposed model in which Mu* is a neutral interstitial located close to the center of Ga—As bond.

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The electronic structure of a muonium defect center is expected to be identical to that of the analogous hydrogen center, except for vibrational effects arising because the positive muon has only $\frac{1}{9}$ the mass of the proton. However, muonium defect centers are readily observed in semiconductors via the technique of muon spin rotation whereas the analogous hydrogen centers have not been observed by use of electron spin resonance (ESR). The spectra of muon spin-precession frequencies have revealed the existence of two quite different paramagnetic centers, normal muonium (Mu) and anomalous muonium (Mu*), in diamond,[1] silicon,[2,3] germanium,[4] and most recently GaAs and GaP.[5] Mu is characterized by a large isotropic muon hyperfine (μhf) interaction, whereas Mu* has a small, highly anisotropic μhf interaction with trigonal symmetry.

Despite years of study, it is still not known what Mu* is—i.e., where the muon is situated, what displacements of the neighboring atoms occur, and what the charge and the electronic state are. Measurements of the μhf interaction alone have not led to a clear picture of the defect. A much better understanding of Mu* should result from measurement of the nuclear hyperfine (nhf) interactions since they characterize the electron-spin density in the region of the surrounding nuclear spins.

In this paper we report precise determination of nhf parameters for Mu* in GaAs by a novel level-crossing-resonance (LCR) technique[6-9] and conventional muon spin rotation. We conclude that the larger nhf interactions originate from the nearest neighbor (nn) Ga and As nuclei on the ⟨111⟩ symmetry axis of Mu*. Comparison of the hf parameters with the free-atom values indicates that 83% of the spin density is located on these two atoms, thus strongly supporting a recently proposed model[10,11] in which Mu* is neutral interstitial muonium located close to the center of a Ga—As bond.

Following Abragam's suggestion for muon LCR experiments,[6] studies of muonium-substituted free radicals[7,8,12] have demonstrated the utility of the method for simple isotropic systems. The LCR spectra for muonium defect centers in crystals are considerably more complicated as a result of anisotropy in the μhf and nhf tensors as well as the presence of nuclear electric quadrupole (neq) interactions for nuclei with spin greater than $\frac{1}{2}$. The present LCR data can be described by use of a system consisting of an electron spin **S**, a muon spin **I**, and a single nuclear spin **J**. The spin Hamiltonian appropriate to Mu* can be written

$$\mathcal{H} = g\mu_B \mathbf{H}\cdot\mathbf{S} - g_\mu \mu_\mu \mathbf{H}\cdot\mathbf{I} + A_\parallel^\mu S_z I_z + A_\perp^\mu (S_x I_x + S_y I_y) - g_n\mu_n \mathbf{H}\cdot\mathbf{J} + A_\parallel^n S_z J_z + A_\perp^n (S_x J_x + S_y J_y) + Q[3J_z^2 - J(J+1)], \quad (1)$$

where **H** is the magnetic field, $A_\parallel^\mu$ and $A_\perp^\mu$ ($A_\parallel^n$ and $A_\perp^n$) are the parallel and perpendicular μhf (nhf) parameters, respectively, and Q is the neq parameter. We have assumed that the μhf, nhf, and neq tensors are all axially symmetric about a common axis $\hat{\mathbf{z}}$, which is one of the crystalline ⟨111⟩ axes, and that the g tensors are isotropic. For each of the electron-spin states, one may derive an approximate effective muon-nuclear spin Hamiltonian, which is valid for high fields and small Q:

$$\mathcal{H}_{\text{eff}} = -g_\mu \mu_\mu \mathbf{H}^\mu \cdot \mathbf{I} - g_n \mu_n \mathbf{H}^n \cdot \mathbf{J} + \tfrac{1}{2} Q[3(\hat{\mathbf{z}}\cdot\hat{\mathbf{n}})^2 - 1][3J_n^2 - J(J+1)], \quad (2)$$

where J_n is the component of **J** along $\hat{\mathbf{n}}$, the unit vector in the direction of $\mathbf{H}^n$. The components of the effective fields

$\mathbf{H}^i$ parallel and normal to $\mathbf{H}$ are respectively

$$H^i_\parallel = H \mp (A^i_\perp \sin^2\theta + A^i_\parallel \cos^2\theta)/2g_i\mu_i, \quad H^i_\perp = \mp (A^i_\perp - A^i_\parallel)\sin 2\theta/4g_i\mu_i, \tag{3}$$

where i equals μ or n, θ is the angle between $\hat{\mathbf{z}}$ and $\mathbf{H}$, and the upper (lower) sign is for M_S positive (negative). The frequencies of the magnetic-dipole transitions for the muon and nuclear spins are given by

$$h\nu_\mu(M_I \leftrightarrow M_I - 1) = g_\mu \mu_\mu H^\mu, \tag{4}$$

$$h\nu_n(M_J \leftrightarrow M_J - 1) = g_n \mu_n H^n - \tfrac{3}{2} Q[3(\hat{\mathbf{z}}\cdot\hat{\mathbf{n}})^2 - 1](2M_J - 1), \tag{5}$$

where M_I (M_J) is the magnetic quantum number for quantization along $\mathbf{H}^\mu$ ($\mathbf{H}^n$). Note that for each value of M_S there is one possible value for ν_μ and $2J$ values for ν_n. The most prominent LCR's occur at applied fields where the muon transition frequency [Eq. (4)] equals one of the nuclear transition frequencies [Eq. (5)],[7,8,12] the same condition as for muon-nuclear cross relaxation.

This experiment was carried out at TRIUMF on the M15 beamline, using low-momentum (28.6 MeV/c) positive muons that were highly polarized (> 95%), either parallel or perpendicular to their momenta. The muons were stopped in a single-crystal wafer of high-resistivity (8×10^7 Ω cm) GaAs supplied by Cominco Ltd., Trail, B.C., Canada. It was maintained at 10 K with one of the primary crystal orientations (⟨100⟩, ⟨111⟩, or ⟨110⟩) along $\mathbf{H}$. The muon spin-rotation frequency spectra in a transverse magnetic field of 1.2 T, where the muon spin is decoupled from all nuclear spins,[13] were in good agreement with the μhf parameters for Mu* reported previously[5] (see Table I), with a typical crystal misalignment of 1°. The LCR's were detected as a reduction in the time-integrated muon decay asymmetry along $\mathbf{H}$, the direction of the initial muon polarization.[7] A square-wave modulation field of ±5 mT was applied, causing the LCR's to appear to be differentiated in the resulting asymmetry-difference spectra (see Fig. 1).

Part of the LCR spectrum for Mu* in GaAs with $\mathbf{H}$ parallel to the ⟨100⟩ direction is shown in Fig. 1(a). It is particularly simple because for this orientation the four possible Mu* centers, corresponding to the four ⟨111⟩ symmetry axes, are all equivalent ($\theta = 54.7°$) and therefore there are fewer LCR's. Also, for $\mathbf{H}$ along a ⟨100⟩ direction $H^\mu_\perp$ is large [see Eq. (3)] and thus ν_μ has an appreciable minimum value. Consequently, there are no level crossings with nuclei which have hf couplings less than about 70 MHz, as there can be for $\theta = 0°$ or 90°. The six prominent LCR's in Fig. 1(a) are all attributed to one ^{75}As nucleus (spin $\frac{3}{2}$ and 100% abundant) on the ⟨111⟩ symmetry axis of Mu*. Each value of M_S gives rise to three resonances which are split by the neq interaction and small off-diagonal terms in $\mathcal{H}_{\rm eff}$ [not shown in Eq. (2)]. The ^{75}As nhf and neq parameters given in Table I were obtained by the fitting of the positions of all the observed LCR's with those predicted from an exact diagonalization of Eq. (1).

For the ⟨110⟩ orientation the crystal was aligned so

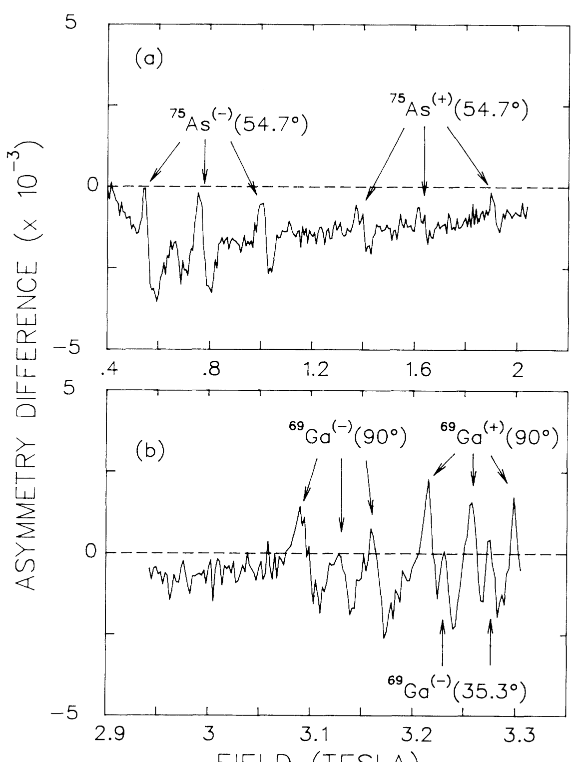

FIG. 1. The level-crossing-resonance spectra of Mu* in GaAs for $\mathbf{H}$ applied along the (a) ⟨100⟩ and (b) ⟨110⟩ directions. The resonances are labeled by the nucleus involved, the sign of M_S, and θ, the angle between the symmetry axis and the magnetic field.

TABLE I. The measured hyperfine and nuclear electric quadrupole parameters for Mu* in GaAs and the inferred s and p atomic spin densities. The s and p spin densities are calculated from $\eta^2\alpha^2 = \frac{1}{3}(A^i_\parallel + 2A^i_\perp)/A_s^{\rm free}$ and $\eta^2\beta^2 = \frac{1}{3}(A^i_\parallel - A^i_\perp)/A_p^{\rm free}$, respectively, where the free-atom values for s and p valence orbitals are obtained from Morton and Preston (Ref. 14). All measured parameters have the same sign.

Nucleus	$A^i_\parallel/h$ (MHz)	$A^i_\perp/h$ (MHz)	Q/h (MHz)	$\eta^2\alpha^2$	$\eta^2\beta^2$
μ^+	218.54(3)	87.87(5)	⋯	0.0294	⋯
^{75}As	563.1(4)	128.4(2)	6.26(7)	0.0186	0.434
^{69}Ga	1052(2)	867.9(3)	0.36(1)	0.0761	0.301

that there were no measurable splittings in the muon precessional frequencies associated with the $\theta=35.3°$ centers. Eight LCR's were observed between 3.0 and 3.3 T [see Fig. 1(b)], all attributed to one ^{69}Ga nucleus (spin $\frac{3}{2}$ and an isotopic abundance of 60.4%) on the Mu* symmetry axis. Six correspond to centers where $\theta=90°$ and two to those with $\theta=35.3°$, as indicated in Fig. 1(b). Four additional ^{69}Ga LCR's and the twelve ^{71}Ga LCR's are predicted to occur in higher fields, beyond the limit of our magnet. However, they are not needed to obtain the hf and neq parameters which are given in Table I.

Effects of nhf interactions were also observed in the frequency spectra in transverse magnetic fields between 0.3 and 0.5 T [see Fig. 2(a) for a ⟨110⟩ spectrum]. In such intermediate fields, the muon is selectively coupled to the nuclei with the larger hf parameters,[15] giving rise to the observed structure. Theoretical spectra [e.g., Fig. 2(b)] were obtained by exact diagonalization of the spin Hamiltonian with use of the parameters in Table I and inclusion of both gallium isotopes. From the striking similarity of the experimental and theoretical spectra, we may conclude that there are no other nuclei with comparable or larger hf parameters and that our assignment of the LCR's is correct.

Many other LCR's were observed in the ⟨111⟩ and ⟨110⟩ spectra in the magnetic field range 0.3–0.8 T, where one expects LCR's from nhf parameters less than about 100 MHz. These smaller nhf couplings will be described in a later publication.

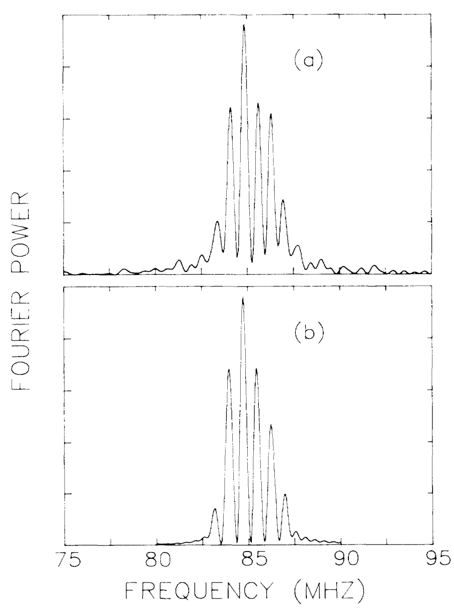

FIG. 2. (a) Resolved nuclear hyperfine structure in the spectrum of muon precessional frequencies for Mu* with $\theta=90°$, $M_S=-\frac{1}{2}$, and the magnetic field (0.30 T) applied parallel to ⟨110⟩. (b) The corresponding theoretical frequency spectrum with use of the parameters in Table I.

Comparison of the measured hf parameters to valence s and p atomic-orbital values[14] gives estimates of the contribution of these atomic orbitals to the defect molecular orbital of the unpaired electron.[16] In this way we obtain a total spin density on the As (Ga) of 45% (38%) with the p-to-s density ratio 23 (4) (see Table I). The large spin densities on both atoms and the appreciable distance between two like atoms along the ⟨111⟩ axis imply that the Ga and As are nn nuclei on this axis. Furthermore, the magnitude of the anisotropic μhf interaction, which is about 1.5 times that from a $2p$ orbital, demonstrates that the μ^+ is within a few atomic radii of this Ga-As pair.

The present results strongly support a recently proposed model[10,11] in which Mu* is a neutral interstitial located near the center of a Ga—As bond. This model predicts that most of the unpaired spin density is located on the two nn nuclei on the ⟨111⟩ symmetry axis and that the muon is near a node in the spin density, all in agreement with the present results. For the bond-centered site to be a minimum in the total energy, there should be an increase in the Ga-As spacing, as has been predicted theoretically for Mu* in diamond and silicon.[10,11] From the measured ratios of p to s spin densities, assuming orthogonal s-p hybridized atomic valence orbitals directed along the internuclear axes and fixed next nn, and estimating s-orbital spin polarization from theoretical calculations on the GeH_3 radical,[17] we estimate that the nn As and Ga are displaced 0.65(17) and 0.14(6) Å away from the bond center, respectively. (The uncertainties arise from spin-polarization effects which are not known accurately.) These displacements imply an increase in the Ga—As bond length of about 32(7)%.

Our results cannot be explained by any other model proposed for Mu* in semiconductors. In the vacancy-associated model[18] the unpaired spin would be primarily on the nn As (Ga) if the muon is in a Ga (As) vacancy. The distance to the closest Ga (As) on the symmetry axis is so great that no significant spin density is expected there. In the hexagonal site model[19] one would expect the spin density to be primarily on the six nn nuclei off the symmetry axis. In the back-bonding model[20] there is no reasonable explanation for the almost equal spin densities on the two nn nuclei on the ⟨111⟩ axis and the small s spin density on the muon.

In conclusion, we have obtained detailed information on the electronic structure of Mu* in GaAs, having used LCR spectroscopy to determine unambiguous and accurate values of all the larger hyperfine parameters. We find that most of the electron spin density is on the nearest-neighbor Ga and As on the ⟨111⟩ symmetry axis. The atomic characters are considerably more p-like than sp^3, thus implying large lattice relaxation. These results strongly support the bond-centered interstitial model for

Mu* in semiconductors and virtually rule out all other models proposed to date.

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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. Hinterman, 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, and Th. Wichert, 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]A. Abragam, C. R. Acad. Sci. Ser. 2 **299**, 95 (1984).

[7]R. F. Kiefl, S. R. Kreitzman, M. Celio, R. Keitel, G. M. Luke, J. H. Brewer, D. R. Noakes, P. W. Percival, T. Matsuzaki, and K. Nishiyama, Phys. Rev. A **34**, 681 (1986).

[8]M. Heming, E. Roduner, B. D. Patterson, W. Odermatt, J. Schneider, Hp. Baumeler, H. Keller, and M. Savic, Chem. Phys. Lett. **128**, 100 (1986).

[9]R. F. Kiefl, Hyperfine Interact. **32**, 707 (1986).

[10]S. F. J. Cox and M. C. R. Symons, Chem. Phys. Lett. **126**, 516 (1986); T. A. Claxton, A. Evans, and M. C. R. Symons, J. Chem. Soc. Faraday Trans. 2 **82**, 2031 (1986).

[11]T. L. Estle, S. Estreicher, and D. S. Marynick, Hyperfine Interact. **32**, 637 (1986), and Phys. Rev. Lett. **58**, 1547 (1987).

[12]P. W. Percival, R. F. Kiefl, S. R. Kreitzman, D. M. Garner, S. F. J. Cox, G. M. Luke, J. H. Brewer, K. Nishiyama, and K. Venkateswaren, Chem. Phys. Lett. **133**, 465 (1987).

[13]R. F. Kiefl, E. Holzschuh, H. Keller, W. Kündig, P. F. Meier, B. D. Patterson, J. W. Schneider, K. W. Blazey, S. L. Rudaz, and A. B. Denison, Phys. Rev. Lett. **53**, 90 (1984).

[14]J. R. Morton and K. F. Preston, J. Magn. Reson. **30**, 577 (1978).

[15]E. Roduner and H. Fischer, Chem. Phys. **54**, 261 (1981).

[16]U. Kaufmann and J. Schneider, in *Festkörperprobleme: Advances in Solid State Physics,* edited by J. Treusch (Vieweg, Braunschweig, 1980), Vol. 20, p. 87.

[17]K. Ohta, H. Nakatsuji, I. Maeda, and T. Yonezawa, Chem. Phys. **67**, 49 (1982).

[18]N. Sahoo, K. C. Mishra, and T. P. Das, Phys. Rev. Lett. **55**, 1506 (1985).

[19]T. L. Estle, Hyperfine Interact. **8**, 365 (1981).

[20]B. D. Patterson, Hyperfine Interact. **18**, 517 (1984).