^{29}Si Hyperfine Structure of Anomalous Muonium in Silicon: Proof of the Bond-Centered Model

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(Received 21 August 1987)

The ^{29}Si hyperfine structure of the anomalous muonium center in silicon has been resolved in muon-spin-rotation spectra. The spectra of the weak ^{29}Si satellite lines show that there are two equivalent Si neighbors on the ⟨111⟩ symmetry axis with large positive *p*-like spin densities. These results, which are confirmed by level-crossing-resonance spectroscopy, establish that anomalous muonium in the group-IV semiconductors is an interstitial muonium located at the bond center.

PACS numbers: 71.55.Eq, 76.70.− r, 76.75.+i

Interest in muonium centers in semiconductors arises because they are simple defects whose electronic structures are closely related to those of hydrogen and the fact that there are no reported observations of isolated paramagnetic hydrogen in a semiconductor. In the group-IV materials, Si, Ge, and diamond, and the group-III-V crystals, GaAs and GaP, two very different types of muonium centers have been seen.[1-5] Normal muonium (or Mu) has an isotropic muon hyperfine (hf) interaction which is roughly half of the free-muonium value. The so-called anomalous muonium center (or Mu*) has a small anisotropic muon hf interaction, axially symmetric about a ⟨111⟩ axis. The accepted model of normal muonium is a neutral interstitial at a tetrahedral interstitial site.[6] Several conflicting models for the structure of Mu* have been proposed, with two receiving considerable theoretical study. In one, Mu* is a substitutional muon (trapped at a vacancy) with an overall charge of $+2e$ (in the group-IV materials),[7,8] and in the other it is a neutral interstitial located at a bond center.[9,10]

Recently we have resolved the nuclear hyperfine (nhf) structure of Mu* in GaAs using level-crossing-resonance (LCR) spectroscopy.[11] The results, which demonstrate that the largest nhf interactions are for a single Ga and a single As on the ⟨111⟩ symmetry axis, provide strong support for the bond-centered (BC) model of Mu* in the zinc-blende structure group-III-V crystals. A more definitive test of the BC model can be made in crystal with the diamond structure, such as Si, since there is inversion symmetry about the bond center. In particular, the BC model predicts that there should be two electronically equivalent Si neighbors on the ⟨111⟩ symmetry axis with large positive spin densities. Verification of this prediction would show that the BC model is valid in the elemental semiconductors. Also, measurements of the Mu* nhf parameters in silicon or diamond are particularly useful for comparison with theory since detailed electronic-structure calculations on these crystals now exist[8,10,12] and more reliable and accurate calculations are anticipated.

We report here a measurement of the ^{29}Si hf parameters of Mu* in silicon, an experiment made difficult by the low natural isotopic abundance (4.7%) of ^{29}Si (spin $=\frac{1}{2}$). The principal experimental approach was to resolve the weak ^{29}Si lines in the muon-spin-rotation frequency spectra in transverse magnetic fields of 5–50 mT. In this field region the muon precessional frequencies of the Mu* centers having a nearest-neighbor (nn) ^{29}Si are split by a few megahertz and have an average position shifted relative to the main lines, corresponding to centers where all nn nuclei are ^{29}Si (spin $=0$ and 95.3% abundant). The ratio between the total amplitude in the satellite lines and main lines is $nf/(1-f)$, where n is the number of equivalent Si neighbors responsible for the splitting and f is the isotopic abundance of ^{29}Si. The frequencies of the satellites give estimates of the nuclear hf parameters. More accurate values, including the signs of the parameters relative to those of the muon, were then obtained with level-crossing-resonance spectroscopy.[11]

The measurements were performed at TRIUMF on the M15 beam line which provides a beam of highly polarized (>95%) positive muons of momentum 28.6

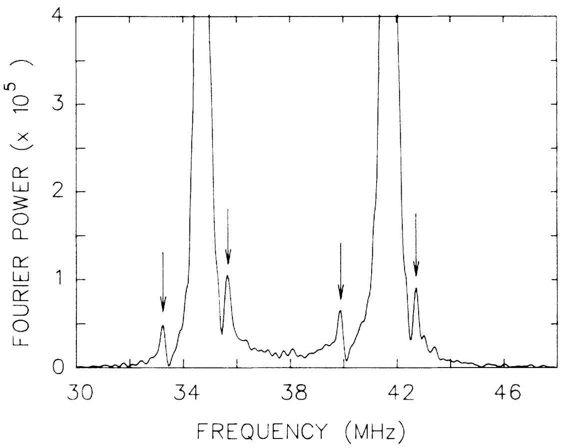

FIG. 1. The muon frequency spectrum in Si with a field of 23.5 mT aligned along a ⟨100⟩ crystal direction. The small satellite lines, indicated by arrows, are due to Mu* centers which have one nearest-neighbor ^{29}Si on the ⟨111⟩ symmetry axis. For presentation clarity the time-differential data were apodized prior to Fourier transformation in order to reduce the ringing from the strong main lines.

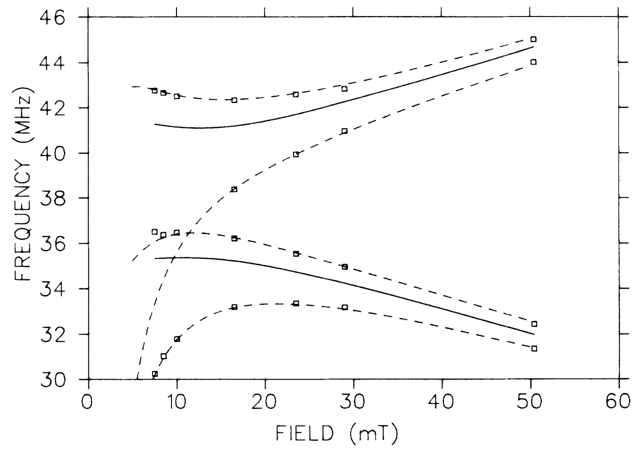

FIG. 2. The magnetic field dependence of the muon-spin-rotation frequencies in Si with the field aligned along the ⟨100⟩ crystal direction. The solid (dashed) curves are predicted if none (one) of the nearest-neighbor nuclei on the symmetry axis is ^{29}Si.

MeV/c. The muons were stopped in a single crystal of float-zoned Si (25-mm diameter by 3 mm thick) maintained at 10 K. Standard time-differential muon-spin-rotation spectra were taken with the external field aligned acurately (within 0.1°) along either a ⟨100⟩ or ⟨111⟩ direction such that there was no detectable broadening of the main muon-spin-rotation lines from misalignment. The Mu* lines are strongest for these orientations since four (or three) of the ⟨111⟩ symmetry axes are equivalent, making an angle $\theta=54.7°$ (or 70.5°) with the magnetic field. Up to 8×10^8 muon decay events were recorded for each spectrum. LCR spectra in selected regions of magnetic field were obtained for the field along ⟨110⟩ and ⟨111⟩ directions corresponding to $\theta=90°$ and 0°, respectively.

One of the muon-spin-rotation frequency spectra is shown in Fig. 1. The amplitudes and frequencies of the lines were obtained by our fitting the finite Fourier transforms of the data by a transform of a theoretical muon polarization function composed of exponentially damped precessional components. The damping rates for all the satellite and main lines were taken to be equal.

Figure 2 shows the Mu* precessional frequencies versus magnetic field for $\mathbf{H}\parallel\langle100\rangle$. The observed and predicted positions for the two main Mu* frequencies, i.e., those for which there are no nn ^{29}Si, are given by the solid curves, where the muon hf parameters are[13,14] $A_\parallel^\mu=-16.82$ MHz and $A_\perp^\mu=-92.59$ MHz. From the locations of the LCR's [72.0(2) and 653.9(5) mT for $\theta=90°$ and 418.9(3) mT for $\theta=0°$], one of which is shown in Fig. 3, we obtained ^{29}Si hf parameter of $A_\parallel^n=-137.5(1)$ MHz and $A_\perp^n=-73.96(5)$ MHz, assuming the nucleus lies on the ⟨111⟩ symmetry axis. With use of these nuclear and muon hf parameters, exact diagonalization of the Mu* spin Hamiltonian including one nn ^{29}Si gives the dashed curves of Fig. 2. The agreement between the observed satellite frequencies and those predicted from the LCR results, plus the absence of any unexplained lines for fields above about 5 mT, demonstrate that the nucleus in question is on the symmetry axis. The measurements of the satellite frequencies alone (squares in Fig. 2) yielded less precise hf parameters and were not accurate enough to determine the sign of $A_\perp^n$. However, these estimates were essential in our finding the LCR's. At the lowest fields (below 5 mT) and for $\theta=70.5°$ a few additional lines were observed which were separated from the main lines by less than 1

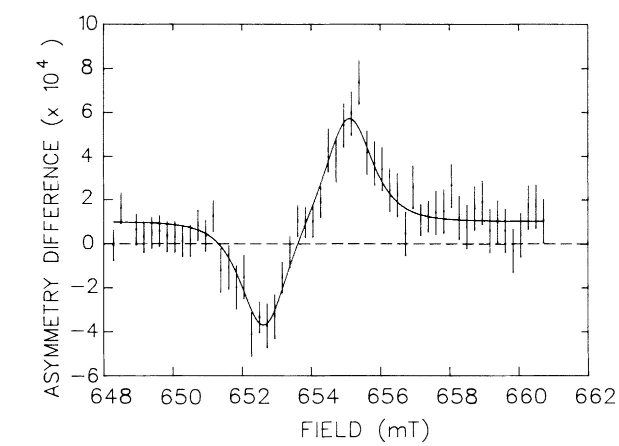

FIG. 3. The high-field level-crossing resonance for Mu* in silicon for those centers whose symmetry axes are at 90° to the field. The resonance occurs at a field where the muon transition frequency is matched to that of a ^{29}Si nearest neighbor (Ref. 11).

MHz. These can be explained by ^{29}Si at a further neighbor site with an effective isotropic ^{29}Si parameter of -20 MHz.

As mentioned above, the number of equivalent Si neighbors on the symmetry axis can be deduced from the total amplitude of the satellite lines relative to that in the two main lines. The spectrum taken at 23.5 mT (see Fig. 1) is the best for this since broadening due to smaller nhf interactions is negligible (the measured damping rate is $\lambda = 0.19\ \mu s^{-1}$) and yet the ^{29}Si lines are well resolved from the main lines. For one or two equivalent neighbors, which are the only possibilities for neighbors on the same ⟨111⟩ axis, the ratio of amplitudes is expected to be 0.0493 or 0.0986, respectively, The measured ratio, 0.109(8), confirms that the splittings arise from ^{29}Si nuclei at two equivalent neighbor sites on the symmetry axis. The amplitudes of the ^{29}Si LCR's are also consistent with two equivalent neighbors.

From the measured ^{29}Si hf parameters one can estimate the s and p atomic spin densities using

$$\eta^2\alpha^2 = \tfrac{1}{3}(A_{\parallel}^{n} + 2A_{\perp}^{n})/A_s^{\text{free}} , \quad (1)$$

$$\eta^2\beta^2 = \tfrac{1}{3}(A_{\parallel}^{n} - A_{\perp}^{n})/A_p^{\text{free}} , \quad (2)$$

where free-atom values, which are negative, were obtained from Morton and Preston.[15] This yields s and p spin densities of $\eta^2\alpha^2 = +0.0207$ and $\eta^2\beta^2 = +0.186$ for each of the two Si neighbors. The two nn's therefore account for a total spin density of 0.413, leaving a substantial amount on further neighbors. With the assumption of sp^3 orbitals and six sites, the smaller splittings seen below 5 mT would account for a total spin density of 0.10, leaving a large part still unobserved. Thus the spin density is significantly delocalized. The spin density on the nn nuclei has considerably more p character than an sp^3 hybridized orbital, as also found for Mu* in GaAs.[11] This suggests a large relaxation of these nuclei away from the bond center, as predicted from structure calculations on BC muonium.[9,10]

In conclusion, we have determined from measurements of ^{29}Si hyperfine structure that there are two equivalent Si neighbor sites on the ⟨111⟩ symmetry axis of Mu* in Si and that the spin density there is large, positive, and mostly p-like. There are only two sites for the muon consistent with the observed inversion symmetry—the bond center and the hexagonal site.[16] (Note that the vacancy-associated model[7,8] is incompatible as is any model involving a single impurity.) Only the bond-centered model has predicted all of the qualitative features of our observations and is supported by detailed structure calculations.[10,12] These results establish beyond any reasonable doubt that Mu* in Si is interstitial muonium located at the bond center.

We wish to thank Keith Hoyle for technical assistance, Stan Dodds and David Noakes for help in data taking, and Jess Brewer for help in data taking and for his critical reading of the manuscript. This work was supported by the National Research and Natural Sciences and Engineering Research Councils of Canada. One of us (T.L.E.) would like to acknowledge support from Robert A. Welch Foundation Grant No. C-1048.

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