and references therein.
[5]J. E. Drumheller, P. H. Amundson, and K. Emerson, J. Chem. Phys. 51, 5729 (1969).
[6]Y. Ajiro and M. Miura, J. Phys. Soc. Jpn. 35, 1787 (1973).
[7]H. Reimann, H. Hagen, F. Waldner, W. Berlinger, and H. Arend, Solid State Commun. 17, 1319 (1975); H. Benner, Appl. Phys. 13, 141 (1977).
[8]H. Yamazaki, J. Phys. Soc. Jpn. 41, 1911 (1976).
[9]M. Tanimoto, T. Kato, and Y. Yokozawa, Phys. Lett. 58A, 66 (1976).
[10]S. Milošević and H. E. Stanley, Phys. Rev. B 6, 1002 (1972).
[11]D. S. Gaunt and C. Domb, J. Phys. C 3, 1442 (1970).

Anomalous Muonium in Silicon

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(Received 21 February 1978)

The anomalous muonium state in Si has been studied with the muon-spin rotation technique as a function of the strength and orientation of the applied magnetic field. It was found that this state is well described by a spin Hamiltonian with axial symmetry about a [111] axis.

The positive muon is a spin-$\frac{1}{2}$ particle with a lifetime of 2.2 μs and a mass of approximately $\frac{1}{9}$ of the proton mass. A muon implanted into an insulator or semiconductor may bind an electron to form muonium (μ^+e^-), a light "isotope" of hydrogen. Precession of interstitial muons and muonium atoms in an external magnetic field is observable using the muon-spin rotation (μSR) technique.[1]

Several μSR experiments have been performed[2-6] in silicon. In these studies a frequency component is always observed which corresponds to the precession of free muons. This so-called "μ^+" component represents muons which fail to capture an electron or which for other reasons find themselves in a diamagnetic environment.

In intrinsic Si samples at low temperatures, a state similar to muonium in vacuum is observed.[4,5] This "normal" muonium ("Mu") is described by a spin Hamiltonian consisting of an isotropic hyperfine interaction and electron and muon Zeeman terms:

$$\mathcal{H}_{\mathrm{Mu}} = A\vec{\mathrm{I}}\cdot\vec{\mathrm{S}} - g_e\mu_B\vec{\mathrm{S}}\cdot\vec{\mathrm{H}} - g_\mu\mu_\mu\vec{\mathrm{I}}\cdot\vec{\mathrm{H}}.$$

The energy eigenvalues of this Hamiltonian are given by the well-known Breit-Rabi diagram. In a μSR experiment, muonium shows itself as characteristic precession frequencies corresponding to the differences between these energy eigenvalues. From the field dependence of the two Mu precession components observable at low fields, it has been determined that $A(\mathrm{Si}) = 0.45A(\mathrm{vacuum})$. This reduction has been interpreted[7] as being due to a "dielectric swelling" of the interstitial muonium atom. The g factor of the muonium electron was found to be approximately equal to 2.

An additional state which we will call "anomalous" muonium (Mu*) has been observed in Si at low temperatures. It shows up as two additional frequencies in the μSR spectra and was the subject of a Letter by Brewer *et al.*[5] Their field-dependent measurements showed that the two Mu* frequencies could be represented by a modified Breit-Rabi diagram. In order to fit the data, $A(\mathrm{Mu}^*)$ was taken to be $0.02A(\mathrm{vacuum})$ and g_e to be -13. It was also found that $A(\mathrm{Mu}^*)$ was slightly dependent on the orientation of the Si crystal with respect to the field. A prediction of this Breit-Rabi description of Mu* is that in zero field a single precession frequency at approximately 90 MHz should be observed.

In order to search for this 90-MHz "muonium heartbeat" signal[8] and to test other features of the Breit-Rabi model, the present investigation was begun at the Swiss Institute for Nuclear Research on a 12-g p-type Si crystal with a doping of approximately 10^{13} cm^{-3}. The crystal was cooled to 30 K in a thin-window stainless-steel

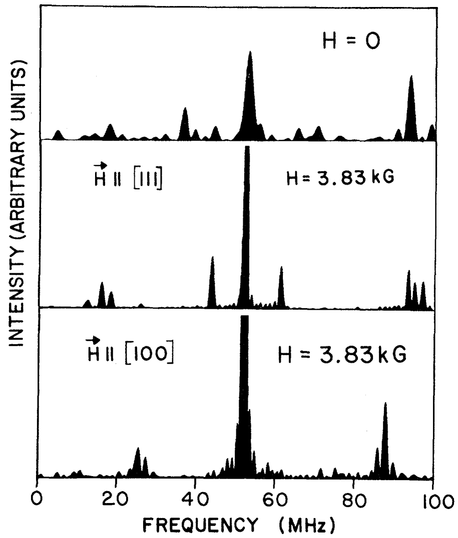

FIG. 1. Typical Fourier transforms of μSR data in Si. In zero applied field, statistically significant peaks at 36, 52, and 92 MHz are observed. At 3.83 kG oriented parallel to the [111] direction, single lines at 43 and 60 MHz and groups of lines at 16 and 95 MHz are observed. With a field parallel to the [100] direction, groups of lines at 25 and 87 MHz are detected. The large peak at 52 MHz in the middle and lower transform arises from the "free" muon precession in the applied field and accidentally coincides with the strongest frequency in zero field.

He-flow cryostat.

A high-statistic run (3×10^7 detected muon decays representing 7 h of running time) at zero applied field yielded the Fourier transform shown in the upper part of Fig. 1. In addition to the expected signal at 92 MHz, two other significant peaks are observed at 36 and 52 MHz which are unexplained by the Breit-Rabi model for Mu*. Field-dependent measurements taken with the [111] axis of the crystal parallel to the applied field showed additional discrepancies with the model: Instead of passing through zero as predicted, the lower strong frequency shows a broad minimum at approximately 3.1 kG (see Fig. 2). Additional weaker lines not explained by the Breit-Rabi theory were also observed as satellites of the μ^+ line.

Measurements as a function of crystal orientation with respect to the external field demonstrated that the observed frequencies are strong functions of orientation (Fig. 3).

The new measurements clearly point out insufficiencies of the isotropic Breit-Rabi Hamiltonian. We have found that a Hamiltonian with an axially symmetric hyperfine interaction[9] might be preferable:

$$\mathcal{H}_{\mathrm{Mu}*} = A_\perp(I_xS_x + I_yS_y) + A_\parallel I_zS_z - g_e\mu_B\vec{S}\cdot\vec{H} - g_\mu\mu_\mu\vec{I}\cdot\vec{H},$$

where the z direction now defines a preferred direction in the crystal. The subsequent analysis of the data showed that this direction coincides with any one of the $\langle 111\rangle$ directions of the diamond lattice of Si.

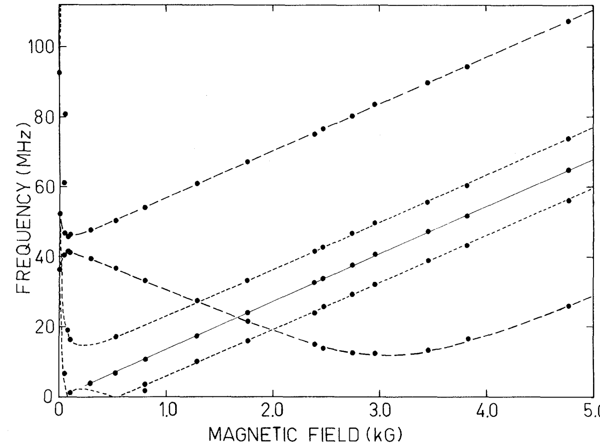

FIG. 2. The experimentally observed precession frequencies are plotted (solid circles) as a function of the external field applied along the [111] direction. Theoretical curves are included for the "μ^+" component (solid line) and for the "Mu*" components. The light (heavy) broken curves correspond to Mu* centers whose symmetry axes make an angle $\theta = 0°$ ($\theta = 70.5°$) with the applied field. The precession components attributable to "normal" muonium (Mu) are not shown.

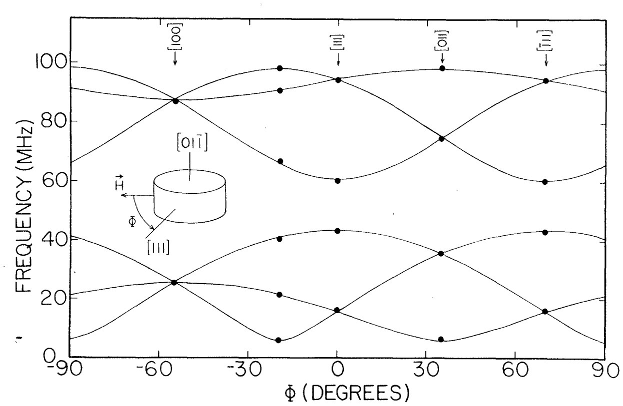

FIG. 3. The experimentally observed Mu* precession frequencies are plotted (solid circles) as a function of the sample orientation in a field of 3.83 kG. The angle Φ defines the direction of the field in the $(01\bar{1})$ plane of the crystal. The solid curves show the theoretical dependence on angle.

The energy eigenvalues of $\mathcal{H}_{\mathrm{Mu}^*}$ as a function of the field are shown in Fig. 4 for $\vec{H}$ parallel to the symmetry or z axis. Different diagrams are obtained for other angles θ between $\vec{H}$ and the z axis. Simple analytical expressions for the eigenvalues are available for $\theta=0$ and $90°$ and in the limits of high and low fields.

In high external fields, $\mathcal{H}_{\mathrm{Mu}^*}$ predicts the existence of two observable precession frequencies ν_{12} and ν_{34} (Fig. 4), one on each side of the free-muon line. One would in general expect four lines on each side of the μ^+ line if Mu* has its symmetry axis in any of the four equivalent ⟨111⟩ directions, but several of these may coincide for certain orientations of the crystal. The center and lower sections of Fig. 1 show Fourier transforms of runs taken at a field of 3.83 kG applied, respectively, along the [111] axis and the [100] axis. For the [111] orientation, one of the ⟨100⟩ directions makes an angle $\theta=0$ with the field, yielding the two satellites of the μ^+ line, and the three remaining ⟨111⟩ directions all lie at $\theta=70.5°$ and yield the groups of lines at 16 and 95 MHz. The small splitting within each of these groups is due to a slight misalignment of the crystal. For the case of the [100] axis parallel to the field, all the Mu* lines fall in two groups, one on each side of the μ^+ line. This follows from the fact that all four axes of the ⟨111⟩ type now make the same angle with the field ($\theta=54.7°$). The results of all the angle-dependent measurements are summarized in Fig. 3.

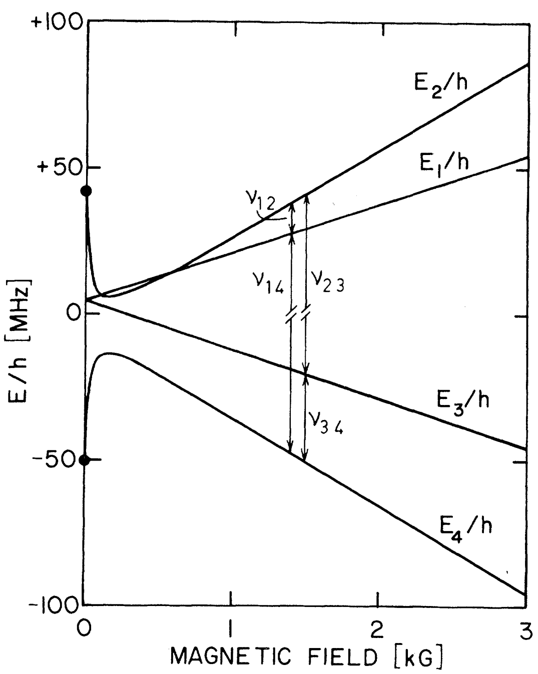

FIG. 4. The energy levels of the axially symmetric spin Hamiltonian $\mathcal{H}_{\mathrm{Mu}^*}$ are plotted as a function of field for the case where the field is parallel to the symmetry axis of the Mu* center. The transitions ν_{14} and ν_{23} have been reduced by a factor 100 for purposes of clarity. This distorts the behavior at very low fields (E_2 and E_4 actually have a horizontal tangent at $H=0$). The only observable precession frequencies in large applied field are ν_{12} and ν_{34}.

In the limit of high field the two observable precession frequencies may be expressed as follows:

$$\begin{pmatrix}\nu_{12}\\ \nu_{34}\end{pmatrix} \approx g_\mu \mu_\mu H \mp \tfrac{1}{2}[A_\perp + (A_\parallel - A_\perp)\cos^2\theta].$$

Estimates for $A_\parallel$ and $A_\perp$ may thus be inferred from the measured frequencies at 4.8 kG (Fig. 2). In the zero-field limit, $\mathcal{H}_{\mathrm{Mu}^*}$ may also be solved analytically to yield the three precession frequencies $|A_\perp|$ and $\frac{1}{2}|A_\perp \pm A_\parallel|$. With the values of $A_\parallel$ and $A_\perp$ estimated from the high-field run, these become 90, 54, and 36 MHz, which are in fair agreement with the observed frequencies in zero field (92, 52, and 36 MHz).

In order to determine accurately the various parameters of $\mathcal{H}_{\mathrm{Mu}^*}$, the eigenvalues were computed by numerical diagonalization of the 4×4 matrices. The parameters resulting from a least-squares fit to the field- and angle-dependent data have the following values:

$|A_\perp| = 92.1 \pm 0.3$ MHz,

$|A_\parallel| = 17.1 \pm 0.3$ MHz,

$A_\perp$ and $A_\parallel$ have the same sign,

$g_\mu = 2.01 \pm 0.01$,

$g_e = -2.2 \pm 0.2$.

The calculated field and angular dependences are shown by the curves in Figs. 2 and 3. The agreement between experiment and theory is excellent.

The success of the Hamiltonian $\mathcal{H}_{\mathrm{Mu}^*}$ in representing the data indicates that Mu* is a paramagnetic state involving a muon with axial symmetry about a [111] crystal axis. The ratio $A_\parallel/A_\perp = +0.19$ implies that the degree of anisotropy is considerable ($A_\parallel/A_\perp = 1$ and 0 for isotropic and X-Y-type interactions respectively).

Several physical models have been proposed for the anisotropic Mu* state. It is possible that the muon interacts with an electronic defect produced during its slowing-down process; impurity-exciton bound states are known[10] to exist in Si. It is regarded as unlikely that the muon interacts with *structural* defects produced during its own slowing-down or that of an earlier muon. This is due to the small number of muon implantations in a μSR experiment (of the order of 10^8, distributed throughout the sample) and to the large kinetic energy required of the muon in order to produce a Si-atom displacement.

A second proposed model assumes that a muonium atom may occupy the symmetric tetrahedral interstitial site in Si and hence contribute to the ("normal") Mu fraction, or it may bind to a neighboring Si atom and occupy a position somewhat closer to any one of the four nearest neighbors. The result would be a polarization of both the muonium and Si atoms with a symmetry axis along a [111] direction.

The final model for Mu* considers another possible stopping site of the muon in Si, namely the hexagonal interstitial site.[11] A muon at such a site is surrounded by a nearly planar hexagon of Si atoms oriented perpendicular to a [111] axis. The desired axial symmetry is thus a feature of the interstitial site itself. The muon-electron dipolar interaction calculated assuming the sharing of the muonium electron among the six nearest-neighbor Si atoms approximately reproduces the anisotropic part $(A_{\parallel} - A_{\perp})$ of $\mathcal{H}_{\mathrm{Mu}^*}$. In this model the Mu component again represents muonium atoms located at the more symmetric tetrahedral sites.

The doping- and temperature-dependent formation probabilities of the three muon states in silicon have been measured. The results will be published elsewhere.

In conclusion, we have found that the introduction of an anisotropic hyperfine interaction has allowed an accurate representation of both the old and new μSR data on the anomalous muonium state in Si. This introduction of anisotropy makes the previous requirement of an electron g factor of 13 unnecessary. A physical model to explain the anisotropy is not yet available, but the new measurements and theory help to define the degree to which muonium states are sensitive to the host lattice.

The authors would like to acknowledge fruitful discussions with F. N. Gygax, J. Keller, W. Baltensperger, and K. A. Müller, and the technical assistance of O. Echt, W. Hofmann, W. Reichart, and K. Rüegg. This work was supported in part by the Swiss National Science Foundation and the Bundesministerium für Forschung und Technologie.

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[1]J. H. Brewer, K. M. Crowe, F. N. Gygax, and A. Schenck, in *Muon Physics*, edited by V. W. Hughes and C. S. Wu (Academic, New York, 1975).

[2]G. Feher, R. Prepost, and A. M. Sachs, Phys. Rev. Lett. 5, 515 (1960).

[3]B. Eisenstein, R. Prepost, and A. M. Sachs, Phys. Rev. 142, 217 (1966).

[4]D. G. Andrianov, E. V. Minaichev, G. G. Myasishcheva, Yu. V. Obukhov, V. S. Roganov, G. I. Savel'ev, V. G. Firsov, and V. I. Fistul', Zh. Eksp. Teor. Fiz. 58, 1896 (1970) [Sov. Phys. JETP 31, 1019 (1970)].

[5]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).

[6]R. F. Johnson, Ph.D. thesis, Lawrence Berkeley Laboratory Technical Report No. LBL-5526 (unpublished).

[7]J. S.-Y. Wang and C. Kittel, Phys. Rev. B 7, 713 (1973).

[8]The concept of a "muonium heartbeat" was suggested to us by L. Grenacs, private communication.

[9]Such an axially symmetric Hamiltonian for Mu* was suggested by Johnson (Ref. 6), but three factors prohibited the correct determination of the parameters involved: (1) the lack of data at low applied fields, (2) the failure to account for the equivalent ⟨111⟩ directions, and (3) incorrect angle-dependent data. A reexamination by one of the present authors (B.D.P.) of x-ray photographs used to orient the samples used in Refs. 5 and 6 disclosed that their [100] orientation was incorrect. When this fact is accounted for, the earlier measurements are in good agreement with the present experiment.

[10]J. R. Haynes, Phys. Rev. Lett. 4, 361 (1960).

[11]K. Weiser, Phys. Rev. 126, 1427 (1962).