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Temperature dependence of the anomalous muonium hyperfine interaction and depolarization rate in silicon

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The temperature dependence of the anomalous muonium hyperfine interaction has been measured in silicon between 5 and 150 K. The hyperfine parameters are observed to decrease with increasing temperature. This is argued to result from interaction of the anomalous muonium center with the silicon host phonons. Above 120 K a rapid increase of the depolarization rate of the anomalous muonium with temperature is observed; these data are consistent with a Raman process causing the increased depolarization.

I. INTRODUCTION

When positive muons are brought to rest in nominally pure Si single crystals, three types of defect centers are generated. One of these consists of μ^+ in a diamagnetic environment, while in the other two the μ^+ interacts with an unpaired electron forming defects similar to muonium. Normal muonium has an isotropic hyperfine interaction constant A which is 45% of the value for muonium in vacuum, while the anomalous muonium center Mu* has a very anisotropic hyperfine interaction which is about 1.5% of the vacuum value.[1,2] The Mu* has axial symmetry about one of the four $\langle 111 \rangle$ crystalline axes. While normal muonium would appear to be an interstitial deep donor the nature of Mu* remains conjectural. Observation of any temperature dependence of the Mu* hyperfine interaction offers some insight into the nature of Mu*. Such temperature dependence was sought but not found earlier.[3,4]

A temperature dependence of the hyperfine interaction can arise from lattice dilation or from interaction with phonons or localized vibrational modes. The former would produce a temperature variation similar to the nonmonotonic variation of the lattice parameter in silicon.[5] On the other hand, since muons are very light they will produce very-high-frequency local modes when implanted in solids. Because of the large activation energy (8500 K by scaling the results of hydrogen incorporated in silicon[6]) no observable low-temperature variation is to be expected from such local modes. Interaction with the much-lower-frequency silicon host phonons, however, produces a monotonic temperature variation which persists to low temperatures.

We report here a temperature dependence of the anomalous muonium hyperfine interaction in silicon. This dependence is somewhat larger than that found for most other paramagnetic centers in crystals. Our measurements show a monotonic variation of the hyperfine parameters which allows us to exclude lattice dilation as the principal cause of the effect. In fact, we find that the temperature dependence is consistent with an interaction with the phonons of the host silicon crystal.

II. EXPERIMENT

The experiments were carried out at the stopped muon channel of the Clinton P. Anderson meson physics facility (LAMPF). Measurements were made on a p-type silicon single crystal with ~5 $\times 10^{11}$ cm^3 electrically active impurities at room temperature, mounted in a liquid-He cold-finger cryostat. The temperature was monitored with a carbon-glass resistance thermometer for the $A_{\parallel}$ determination at 1000 G and a silicon diode for the $A_{\perp}$ experiment at 150 G. In each experimental run time-differential transverse-field muon-spin-rotation (μSR) data were accumulated in four histograms from which the precessional frequencies and their relaxation rates were extracted by multifrequency fits. With the magnetic field nearly along a $\langle 111\rangle$ axis, signals are seen not only from centers approximately parallel to the field but also from centers at about 70.5° to the field. Similarly, if the magnetic field is applied nearly along $\langle 110\rangle$, two kinds of centers are seen which are nearly perpendicular to the field, as well as two that are at an angle of approximately 35.3° to the field. The signals due to these off-axis centers were used to estimate the error in the crystal alignment with respect to the magnetic field, as discussed below.

III. DETERMINATION OF THE HYPERFINE INTERACTION FROM THE OBSERVED Mu* PRECESSIONAL FREQUENCIES

In this experiment the magnetic field was applied nearly parallel to a $\langle 111\rangle$ axis (and thus the symmetry axis of one of the four differently oriented Mu* centers) or nearly parallel to a $\langle 110\rangle$ axis (and thus nearly perpendicular to two of the four Mu* centers). Explicit expressions for the energies and the μSR frequencies can be obtained as shown below. Including a possible axially symmetric electronic g tensor, the spin Hamiltonian will be, in general,

$$\mathcal{H}=g_{\parallel}\mu_B H_z S_z+g_{\perp}\mu_B(H_xS_x+H_yS_y)$$
$$-g_\mu\mu_\mu\vec{\mathrm{H}}\cdot\vec{\mathrm{I}}+A_{\parallel}S_zI_z+A_{\perp}(S_xI_x+S_yI_y)\,.$$

Case (a). If the magnetic field is *parallel* to z, the Hamiltonian becomes

$$\mathcal{H}=g_{\parallel}\mu_B HS_z-g_\mu\mu_\mu HI_z+A_{\parallel}S_zI_z+\tfrac{1}{2}A_{\perp}(S_+I_-+S_-I_+)$$

in terms of the usual spin raising and lowering operators. If we label the eigenvalues in the order of their energies at large magnetic field, then the solutions for $g_{\parallel}$ and g_μ positive are

$$E_{3(2)}=\tfrac{1}{4}A_{\parallel}\pm(\tfrac{1}{2}g_{\parallel}\mu_B H-\tfrac{1}{2}g_\mu\mu_\mu H)\,,$$
$$E_{4(1)}=-\tfrac{1}{4}A_{\parallel}\pm\tfrac{1}{2}[(g_{\parallel}\mu_B H+g_\mu\mu_\mu H)^2+A_{\perp}^2]^{1/2}\,.$$

If the hyperfine parameters satisfy

$$1>\left|\frac{A_{\parallel}}{A_{\perp}}\right|>\frac{2(g_{\parallel}\mu_B g_\mu\mu_\mu)^{1/2}}{g_{\parallel}\mu_B+g_\mu\mu_\mu}$$

(the last expression is equal to 0.1385 for $g_{\parallel}$ equal to 2), which undoubtedly holds for anomalous muonium in silicon, then levels 3 and 4 cross for two different values of the magnetic field. It is levels 1 and 2 which cross if $A_{\parallel}<0$, but the conclusions we draw are unchanged. If the magnetic field satisfies

$$H>\frac{1}{4g_{\parallel}\mu_B g_\mu\mu_\mu}\{|A_{\parallel}|(g_{\parallel}\mu_B-g_\mu\mu_\mu)$$
$$+[A_{\parallel}^2(g_{\parallel}\mu_B+g_\mu\mu_\mu)^2-4g_{\parallel}\mu_B g_\mu\mu_\mu A_{\perp}^2]^{1/2}\}\,,$$

then level 4 is above level 3 and the two μSR frequencies are given by

$$h\nu_{43}=-\tfrac{1}{2}g_{\parallel}\mu_B H+\tfrac{1}{2}g_\mu\mu_\mu H-\tfrac{1}{2}A_{\parallel}$$
$$+\tfrac{1}{2}[(g_{\parallel}\mu_B H+g_\mu\mu_\mu H)^2+A_{\perp}^2]^{1/2}\,,$$
$$h\nu_{21}=-\tfrac{1}{2}g_{\parallel}\mu_B H+\tfrac{1}{2}g_\mu\mu_\mu H+\tfrac{1}{2}A_{\parallel}$$
$$+\tfrac{1}{2}[(g_{\parallel}\mu_B H+g_\mu\mu_\mu H)^2+A_{\perp}^2]^{1/2}\,.$$

For $g_{\parallel}=2$ the magnetic field must exceed a value of about 510 G for Mu* in Si for these results to be valid, a condition clearly satisfied by the field of 1000 G used for this part of the present experiment. In this case, we find that

$$h\nu_{21}-h\nu_{43}=A_{\parallel}\,,$$

so that $A_{\parallel}$ is found by taking the difference between the μSR frequencies.

Case (b). For the magnetic field *perpendicular* to z, the spin Hamiltonian takes a convenient form if we take the direction of the field to be the x axis, transform x to z, z to y, and y to x, and write the results in terms of spin raising and lowering operators:

$$\mathcal{H}=g_{\perp}\mu_B HS_z-g_\mu\mu_\mu HI_z+A_{\perp}S_zI_z$$
$$+\tfrac{1}{4}(A_{\perp}-A_{\parallel})(S_+I_++S_-I_-)$$
$$+\tfrac{1}{4}(A_{\perp}+A_{\parallel})(S_+I_-+S_-I_+)\,.$$

Labeling levels as before, we have

$$E_{3(2)}=\tfrac{1}{4}A_{\perp}\pm\tfrac{1}{2}[(g_{\perp}\mu_B H-g_\mu\mu_\mu H)^2+\tfrac{1}{4}(A_{\perp}-A_{\parallel})^2]^{1/2}\,,$$
$$E_{4(1)}=-\tfrac{1}{4}A_{\perp}\pm\tfrac{1}{2}[(g_{\perp}\mu_B H+g_\mu\mu_\mu H)^2+\tfrac{1}{4}(A_{\perp}+A_{\parallel})^2]^{1/2}\,.$$

Level 3 is above level 4 for Mu* in Si since

$$\frac{A_{\perp}}{A_{\parallel}}>\frac{2g_{\perp}\mu_B g_\mu\mu_\mu}{g_{\perp}^2\mu_B^2+g_\mu^2\mu_\mu^2}\,,$$

as long as the magnetic field satisfies

$$H<\frac{1}{2g_{\perp}\mu_B g_\mu\mu_\mu}[(g_{\perp}\mu_B-g_\mu\mu_\mu)^2A_{\perp}^2$$
$$+2g_{\perp}\mu_B g_\mu\mu_\mu(A_{\perp}-A_{\parallel})A_{\perp}]^{1/2}\,,$$

which for $g_{\perp}=2$ is about 3391 G. This is satisfied by the 150-G field used in the second part of our experiment, so that the two μSR frequencies are given by

$$h\nu_{34}=\tfrac{1}{2}A_{\perp}+\tfrac{1}{2}[(g_{\perp}\mu_B H-g_\mu\mu_\mu H)^2+\tfrac{1}{2}(A_{\perp}-A_{\parallel})^2]^{1/2}$$
$$-\tfrac{1}{2}[(g_{\perp}\mu_B H+g_\mu\mu_\mu H)^2+\tfrac{1}{4}(A_{\perp}+A_{\parallel})^2]^{1/2}\,,$$

$$h\nu_{21} = \tfrac{1}{2}A_\perp - \tfrac{1}{2}[(g_\perp \mu_B H - g_\mu \mu_\mu H)^2 + \tfrac{1}{4}(A_\perp - A_\parallel)^2]^{1/2} + \tfrac{1}{2}[(g_\perp \mu_B H + g_\mu \mu_\mu H)^2 + \tfrac{1}{4}(A_\perp + A_\parallel)^2]^{1/2} .$$

Consequently, in this case, we find that

$$h\nu_{21} + h\nu_{34} = A_\perp ,$$

hence $A_\perp$ is found from the sum of the μSR frequencies. It is seen that our method of determining $A_\perp$ and $A_\parallel$ does not require precise measurement of the magnetic field.

Since the silicon crystal was not aligned exactly with the magnetic field, some small corrections are required. For arbitrary orientation, the exact μSR frequencies can only be found numerically; however, for small misalignments one can obtain relatively simple and accurate expressions using perturbation theory. These corrections are independent of the direction of misalignment. The largest correction for the field nearly perpendicular to the axis [case (b)] gives

$$h\nu_{34} + h\nu_{21} = A_\perp - \tfrac{1}{2}\theta^2 A_\perp , \qquad (1)$$

where θ is the angle the magnetic field makes with the plane perpendicular to the anomalous muonium axis. The correction to $A_\parallel$ [case (a)] is more complicated:

$$h\nu_{21} - h\nu_{43} = A_\parallel - \frac{\theta^2}{2} \frac{[\frac{1}{4}A_\perp^2 A_\parallel - (A_\perp - A_\parallel)(g_\mu \mu_\mu H)^2]}{(g_\mu \mu_\mu H)^2 - \frac{1}{4}A_\parallel^2} . \qquad (2)$$

IV. RESULTS AND DISCUSSION

The variation of the parallel and perpendicular components of the Mu* hyperfine interaction with temperature is shown in Fig. 1. Both $A_\perp$ and $A_\parallel$ decrease monotonically with increasing temperature, being reduced by 1.3% and 0.8%, respectively, at 150 K. These changes fall nearly within the range of values, 0.15–1.1%, found from (EPR) data for various paramagnetic centers.[7]

These explicit temperature effects are a manifestation of the spin-phonon interaction. Simanek and Orbach[8] proposed that the phonons induced s-like admixtures into the ground $3d^5$ configuration in order to explain the MgO:Mn^{2+} results. The resulting temperature dependence of the hyperfine interaction is then determined by the time average of the phonon-induced contribution. Such phonon-induced contributions are proportional to the square of the strain. For a Debye phonon spectrum, the thermal average of the square of the strains produces a hyperfine interaction in the long-wavelength limit of

$$A(T) = A(0)\left(1 - CT^4 \int_0^{\Theta_D/T} \frac{x^3}{e^x - 1} dx\right) , \qquad (3)$$

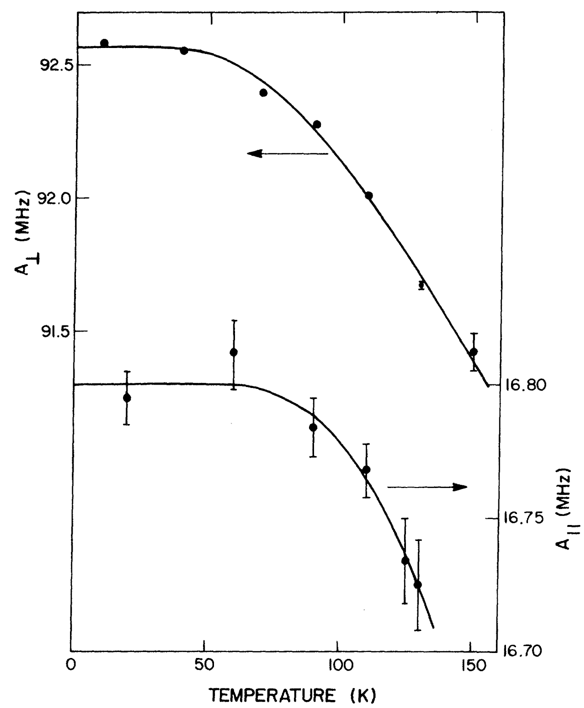

FIG. 1. Temperature variation of the parallel $A_\parallel$ and perpendicular $A_\perp$ components of the anomalous muonium hyperfine interaction in silicon.

where C is a constant determined by the orbit-lattice interaction and Θ_D is the Debye temperature. This equation was found to fit the MgO:Mn^{2+} temperature dependence[9] very well, even though the value of C was not accurately given by the model calculation.

Alternatively, if the thermal average of the square of the strain is obtained from an Einstein oscillator, as would be the case if a single phonon or local mode were the principal cause of the temperature variation, then the hyperfine interaction is given by the expression[10]

$$A(T) = A(0)\left[1 - C\left(\coth\frac{h\nu}{kT} - 1\right)\right] , \qquad (4)$$

where $h\nu$ is the energy of the interacting vibrational mode.

We have found that both Eqs. (3) and (4) can fit the observed temperature dependence of the hyperfine interaction in anomalous muonium in Si. From Eq. (3) a least-squares fit yields

$A_\perp(0) = 92.549 \pm 0.004$ MHz ,

$C_\perp = (7.136 \pm 0.074) \times 10^{-12}\ \mathrm{K}^{-4}$, $\chi^2/\nu = 26$,

$A_\parallel(0) = 16.804 \pm 0.007$ MHz ,

$C_\parallel = (3.128 \pm 0.624) \times 10^{-12}\ \mathrm{K}^{-4}$, $\chi^2/\nu = 0.44$

assuming a Debye temperature of 640 K for Si.[11]

A statistically better fit for $A_\perp$ is obtained by allowing the Debye temperature to vary to an effective Debye temperature Θ'_D:

$$A_\perp(0) = 92.573 \pm 0.005 \text{ MHz},$$
$$C_\perp = (11.743 \pm 0.732) \times 10^{-12} \text{ K}^{-4},$$
$$\Theta'_D = 415 \pm 17 \text{ K}, \; \chi^2/\nu = 11.$$

On the other hand, the parameters corresponding to the best fit to Eq. (4) are

$$A_\perp(0) = 92.569 \pm 0.005 \text{ MHz}, \; C_\perp = 0.0300 \pm 0.002,$$
$$h\nu_\perp = 260 \pm 8 \text{ K}, \; \chi^2/\nu = 15.5,$$
$$A_\parallel(0) = 16.800 \pm 0.008 \text{ MHz}, \; C_\parallel = 0.1705 \pm 0.302,$$
$$h\nu_\parallel = 565 \pm 223 \text{ K}, \; \chi^2/\nu = 0.44.$$

The $T = 0$ values of both types of fit agree very closely, and it is not possible to decide between the two formulas from the quality of the fit. The large χ^2/ν for $A_\perp$ is probably a result of the drift in the electronics for time-to-digital conversion mentioned below. However, from the energies of the phonons found to be involved in the temperature dependence, it is clear that interaction with the silicon host phonons is the dominant cause of the variation, as opposed to any localized phonon mode of the muonium itself. Unfortunately, the phonon frequency in the fit to a single phonon mode is not accurately enough determined to assign it to any particular singular point in the silicon phonon spectrum.

The hyperfine parameters $A_\parallel$ and $A_\perp$ can be corrected for misalignment using Eqs. (1) and (2). For $A_\perp$ the angle θ was determined approximately from the splitting of the μSR lines from the centers making an angle of nearly 35° with the field direction. These centers produced lines near 31 and 25 MHz in a 150-G magnetic field. The former were split by about 1.29 MHz, which according to computed eigenvalues of the spin Hamiltonian corresponds to a 1.1° deviation of the magnetic field out of the (100) plane which bisects the axes of the two centers. The corrected value of $A_\perp(0)$ is obtained by dividing the measured value by 0.99982, but no change in the temperature dependence results. This correction is less than the uncertainty in the final value of $A_\perp(0)$. A small tilt from ⟨110⟩ in the (100) plane may also exist but should result in a negligible correction. For $A_\parallel$ the misalignment angle θ was determined from the three centers making angles of 70.5° with the magnetic field. These centers give lines at about 57 and 30 MHz in 1 kG. The structure at 57 MHz was ambiguous and not analyzed in detail, while the 30-MHz lines were doublets, not triplets, with a 0.345-MHz splitting which, according to numerical computations, corresponds to a 1.3° tilt toward ⟨110⟩. The values of $A_\parallel(0)$ can be corrected by subtracting 0.012 MHz from the uncorrected value and again no effect on the temperature dependence results within the experimental error. This correction is of the order of the uncertainty in the final value of $A_\parallel(0)$.

Analysis of the temperature dependence of the μSR frequencies from the centers which make angles of about 70.5° with the field give results consistent with the temperature dependence obtained for $A_\perp$. Similar analysis of the 35° centers was not possible due to the quality of the data.

In addition to the statistical errors in the derived quantities, there was a significant drift noticed in the time-to-digital conversion electronics during the experiment, which adds a contribution of one part in 2000 to the probable error of the $T = 0$ values. Therefore our best estimates are

$$A_\parallel(0) = 16.788 \pm 0.011 \text{ MHz},$$
$$A_\perp(0) = 92.59 \pm 0.05 \text{ MHz}.$$

This drift is also probably the cause of the large χ^2 per degree of freedom for $A_\perp(T)$.

If we assume that $A_\perp$ and $A_\parallel$ are due only to s and p orbitals on the μ^+, for axial symmetry each contributes as follows[12]:

$$A_\parallel = A_s + 2A_p, \; A_\perp = A_s - A_p,$$
$$A_s = \tfrac{1}{3}(A_\parallel + 2A_\perp), \; A_p = \tfrac{1}{3}(A_\parallel - A_\perp).$$

Hence we may determine the temperature dependence of A_s and A_p from the measured values of $A_\parallel$ and $A_\perp$. Both A_s and A_p show the same monotonic temperature variation as $A_\parallel$ and $A_\perp$ in Fig. 1, the relative change being ~1% out to 130 K for both. The 0 K values are $A_s = 67.32 \pm 0.04$ MHz and $A_p = -25.27 \pm 0.02$ MHz, using our best estimates for $A_\parallel$ and $A_\perp$. The negative value of A_p means the electron density lies in a plane perpendicular to the defect axis. For example, if the Mu* is located at the hexagonal interstitial site,[2] the sign and magnitude of A_p are given by a classical dipole calculation for an electron on the puckered hexagon of nearest neighbors lying in a plane perpendicular to the defect axis. However, a more detailed model is required to explain all of the properties of Mu* located at this interstice.[13]

Analysis of the $A_\perp$ μSR data also yields the depolarization rate of anomalous muonium in silicon as a function of temperature. The rate is nearly constant at ~0.1 μsec^{-1} to about 120 K, where it increases very sharply. This increase is very similar to that obtained at SIN (Swiss Institute for Nuclear Research) by Boekema *et al.*[14] and a semilogarithmic plot of depolarization

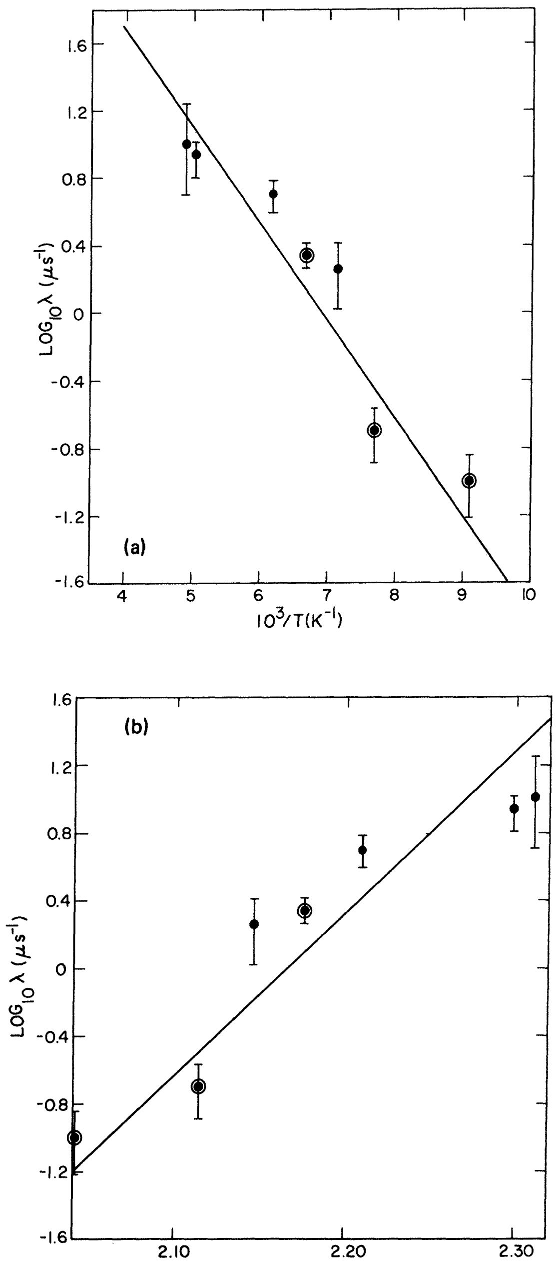

FIG. 2. Temperature dependence of the anomalous muonium depolarization rate in silicon plotted against the inverse temperature showing the possible existence of an activation energy (upper) (a), and plotted against $\log_{10}T$ with the solid line representing a T^9 law (lower) (b). The circled points are the LAMPF data and the others are SIN data.

rate against inverse temperature shows an activation energy of the depolarization rate of 110 ± 35 meV for the combined LAMPF and SIN data, shown in Fig. 2(a). However, since our data were taken on 30 000-Ω cm resistivity Si with approximately 5×10^{11} cm^3 electrically active impurities, and the SIN data were taken on 450-Ω cm Si with 40 times more electrically active impurities, a line through the two sets of data is not to be expected if free carriers are the cause of the Mu* depolarization. Instead our data should be displaced vertically from the SIN data by at least ten standard deviations, which is clearly not the case. The results of the two experiments, therefore, are not in favor of depolarization by free carriers even though the apparent activation energy is rather reasonable.

Another possible source of Mu* depolarization is phonon-induced relaxation via a Raman process which predicts a T^9 temperature variation for an $S=\frac{1}{2}$ system. Figure 2(b) shows a log-log plot of depolarization rate against temperature with a solid line illustrating a T^9 law. The combined data show reasonable agreement with this prediction of a Raman process.

The depolarization rates observed for all four orientations measured show no clear angular variation. Furthermore, since our data were taken at 150 G and 1 kG and the SIN data[14] were taken at 4.5 kG, we can also conclude that the depolarization rate is independent of magnetic field strength.

Finally, we note parenthetically that we have observed the sense of precession of the $\parallel$ and $\perp$ Mu* signals. The precession sense agrees with the theoretical predictions: In the $A_{\parallel}$ measurement both $\parallel$ signals precess in the same sense as the μ^+, while in the $A_{\perp}$ measurement the lower frequency $\perp$ signal (ν_{34}) has the reverse sense of precession, corresponding to level 3 being higher in energy than level 4. The one normal muonium signal observed precesses opposite to μ^+.

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