A detailed analysis of the results for the various models will be given in a forthcoming paper.

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# Quadrupole Splitting of Muonium Precession in $\alpha$-Quartz

Jess H. Brewer and Douglas S. Beder
*Department of Physics, University of British Columbia, Vancouver, British Columbia V6T1W5, Canada*

and

David P. Spencer
*Department of Chemistry, University of British Columbia, Vancouver, British Columbia V6T1W5, Canada*

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Muonium-spin–rotation experiments at low fields (< 75) show evidence for the interaction of the interstitial charge distribution of crystalline quartz with the intrinsic electric quadrupole deformation of the triplet ground state of the muonium atom.

The first direct observation of triplet ($F = 1$) muonium (Mu) precession in a solid was achieved in 1968 using positive muons stopped in fused quartz ($SiO_2$) in a 7.2-G magnetic field.[1] The apparent relaxation rate of the Mu polarization was seen to be faster in crystalline $SiO_2$ than in fused $SiO_2$. Since then, fused $SiO_2$ has been routinely used to calibrate the efficiency of other materials for Mu formation—the $\mu^+$ has a higher probability of forming Mu in $SiO_2$ than in any other known solid. Fused quartz was also the first medium in which "two-frequency precession" of Mu was observed[2] in magnetic fields $\geq 50$ G. This phenomenon, due to a quadratic Zeeman term in the energy of the $M = 0$ states, has been used to measure the strength of the Fermi contact interaction between $\mu^+$ and $e^-$ spins in the strongly coupled "deep" Mu atom in $SiO_2$, Ge, and Si.[2-4] This interaction is normally isotropic, but in Si crystals a dramatic anisotropy has been observed in the phenomenological hyperfine interaction of a second, weakly coupled, "shallow" Mu* (anomalous muonium) state.[5]

We have now observed a new phenomenon: The precession of triplet Mu in a quartz crystal is split into two clearly resolved frequencies whose difference is as large as 0.79 MHz in an applied field of 3.3 G, where the usual splitting due to the quadratic Zeeman effect should be only 0.0047 MHz. Moreover, the splitting is independent of field strength but depends dramatically upon the orientation of the crystal in the field. As we

 

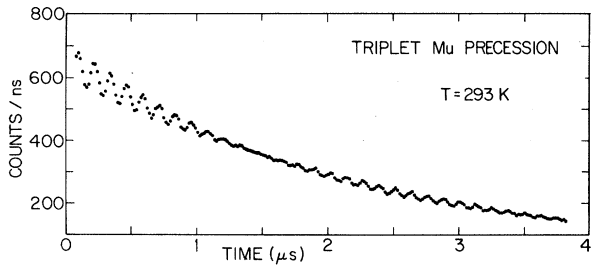


FIG. 1. A high-statistics time spectrum for Mu in $\alpha$-$SiO_2$ at 6.3 G ($\hat{c}$ axis $\perp$ magnetic field). Compared with Eq. (1). "Beats" are obvious.

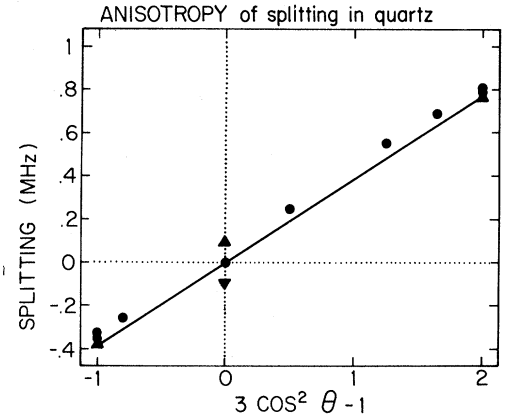


FIG. 2. Angular dependence of the splitting $\Delta\nu$ between the two observed transition frequencies for Mu in $\alpha$-$SiO_2$: $\theta$ is the angle between the $\hat{c}$ axis of the crystal and the applied magnetic field (6.3 G) for round points and 3.3 G for triangular points). Statistical uncertainties are smaller than the size of the points.

shall see, this effect is due to an (electric) quadrupolar interaction between the $F=1$ state of Mu and the crystalline field.

The quartz sample, obtained from Sawyer Research Products, Inc., was optical-grade $d$-$\alpha$-$SiO_2$, grown from solution on a seed crystal, and later cut (seed free) into a cube 3.81 cm on a side, with one face perpendicular to the $\hat{c}$ axis. The magnetic field direction was measured *in situ* with a dip needle, and the crystal was then oriented in the field using a goniostat. This allowed the angle $\theta$ between the $\hat{c}$ axis of the crystal and the applied field to be set within $\pm 2°$ for fields down to about 2 G. A beam of 175-MeV/$c$ polarized positive muons from the $M20$ channel at TRIUMF was stopped in the crystal in the apparatus described by Fleming *et al.*[6] (without the gas target can) and muonium-spin-rotation time spectra were accumulated by conventional techniques.[3] A high-statistics time spectrum is shown in Fig. 1. For several fields and a number of crystal orientations, the spectra were fitted by $\chi^2$ minimization with the form

$$N(t)=\text{const}+N_0\exp(-t/\tau_\mu)\{1+A_{\mathrm{Mu}}e^{-\lambda t}[\cos(2\pi\nu_1 t+\varphi)+\cos(2\pi\nu_2 t+\varphi)]+A_\mu\cos(-2\pi\nu_\mu t+\varphi)\}, \quad (1)$$

where a constant background term has been included, $N_0$ is a normalization factor, $A_{\mathrm{Mu}}$ and $A_\mu$ are the muonium and free-muon precession amplitudes, $\lambda$ the Mu relaxation rate, $\nu_1$ and $\nu_2$ the two frequencies of Mu precession, $\varphi$ the common initial phase of all three precession signals, and $\nu_\mu$ the free-muon precession frequency, held equal to $(\nu_1+\nu_2)/206$.

The splitting frequency $\Delta\nu=\nu_2-\nu_1$ is plotted as a function of $3\cos^2\theta-1$ in Fig. 2. Some liberty has been taken in plotting the left-hand points as negative splittings, since only the absolute value can be measured. This introduces a sign ambiguity in the 3.3-G point at $3\cos^2\theta-1=0$, which is therefore plotted twice. The overall linearity is deemed good enough to justify this procedure. Figure 2 also shows that the splitting does not depend on field between 3.3 and 6.3 G.

These results show that Mu in $\alpha$-$SiO_2$ experiences a hyperfine interaction which is anisotropic, with a preferred direction fixed in the crystal lattice. This is a familiar situation in EPR, where (for cases with axial symmetry) such phenomena are described by an anisotropic spin Hamiltonian of the form

$$H=-(g_\mu\mu_\mu\vec{\mathbf{I}}+g_e\mu_{\mathrm{B}}\vec{\mathbf{S}})\cdot\vec{\mathbf{B}}+h\nu_0\vec{\mathbf{I}}\cdot\vec{\mathbf{S}}+h\,\Delta\nu_0(I_z S_z), \quad (2)$$

where $\vec{\mathbf{I}}$ and $\vec{\mathbf{S}}$ are the spins of the muon and electron, respectively, $\nu_0$ is the isotropic part of the hyperfine frequency, and $\Delta\nu_0$ is the hyperfine anisotropy. The $\hat{z}$ direction is fixed in the crystal (here $\hat{z}=\hat{c}$). Interestingly enough, the Hamiltonian used successfully to describe the Mu* state in Si can be written in exactly the same form.[5] However, the magnitudes of the fitted quantities $\nu_0$ and $\Delta\nu_0$ are grossly different. For Mu* in Si, $\nu_0$ is only about 2% of the value for Mu in vacuum, and $\Delta\nu_0=-0.82\nu_0$. To check for a difference between $\nu_0$ for crystalline $SiO_2$ and that for fused $SiO_2$ (or vacuum), a measurement was made on the new sample at $3\cos^2\theta-1=0$ in a 77-G field. The observed quadratic Zee-

man splitting was consistent with the value obtained in fused $SiO_2$, implying a $\nu_0$ value equal (within an uncertainty of about 7%) to the vacuum value, 4463 MHz.[2] Thus Mu in quartz is described by Eq. (2) with $\nu_0 = 4463 \pm 300$ MHz and $|\Delta\nu_0| = 0.79 \pm 0.03$ MHz.

EPR experiments[7] on H atoms in $\alpha$-$SiO_2$ at 77 K show that the most common site (interstital, in $\hat{c}$-axis channels, between Si atoms) gives an anisotropic spin Hamiltonian with values similar to ours for Mu, except without axial symmetry. However, at room temperature, we expect rapid diffusion of Mu along $\hat{c}$-axis channels, averaging over various interstitial locations. Consequently we have tentatively assumed axial symmetry for our theoretical interpretation. Future experiments will address the question of axial asymmetry, which was overlooked in the present experiment.

Our interpretation of these results is based on the presence of an $L = 2$ component in the spin-triplet ground state of Mu *in vacuo*; this originates with the tensor hyperfine interaction,[8-10] and endows Mu with an intrinsic quadrupole moment,

$$Q/e = (3m_e m_\mu)^{-1} = 2.4\times 10^{-24}\ \mathrm{cm}^2. \tag{3}$$

We can take the $F = 1$ state vector to be

$$|F=1,M\rangle = |L=0;S=1,M\rangle + \textstyle\sum_{M'} C(121/M',M-M')|L=2,M-M'\rangle \otimes |S=1,M'\rangle\,, \tag{4}$$

where perturbation theory provides the $L = 2$ wave function[9,10]

$$\varphi(L=2,M) = \frac{-e^2}{3(m_e+m_\mu)}\frac{a_0^{1/2}}{5}\,Y_{2M}(\Omega)\exp(-r/a_0)F(r), \quad F(r) = \frac{1+r/3a_0}{ra_0^2}, \quad a_0 = \text{Bohr radius}. \tag{5}$$

From this wave function one discovers that fully half the quadrupole moment lies beyond two Bohr radii!

Now, if we simulate the lattice electrostatic potential (seen by our Mu in an interstitial "channel" in quartz) by a spin-independent axially symmetric potential $V(\vec{r})$, then we obtain, to lowest order in the hyperfine interaction,

$$\langle F=1,M|V(\vec{r})|F=1,M'\rangle = \delta_{MM'}[\langle L=0|V(\vec{r})|L=0\rangle + 2C(121/M,0)\langle L=0|V(\vec{r})|L=2\rangle]. \tag{6}$$

The second term, dependent on the atom's orientation, represents the interaction energy of the *intrinsic* quadrupolar deformation of Mu, and is proportional to the characteristic quadrupole factor, $C(121/M,0)$. If one then calculates matrix elements to second order in $V(\vec{r})$, representing the interaction of the *lattice-induced* deformation, one again finds precisely the same characteristic orientation dependence.

Finally, introducing a magnetic field $\vec{B}$ oriented at an angle $\theta$ to the crystal's $\hat{c}$ axis, one obtains a Hamiltonian (2) which can be straightforwardly diagonalized. For weak ($\lesssim 10$ G) $\vec{B}$ field, one can work within the subspace of $F = 1$ states and obtain two precession frequencies whose difference is independent of $B$:

$$\Delta\nu = (12/\sqrt{10})\langle L=0|V(\vec{r})|L=2\ (\text{hyperfine}),M=0\rangle P_2(\cos\theta)\,, \tag{7}$$

provided that $|\vec{B}|$ is well above the value for energy-level crossover—which means, in the present experiment, $|\vec{B}| > 0.284$ G. In this case, explicit solution shows that equal-amplitude beating should occur.

It is instructive to consider two plausible "toy" models for the charge density $\rho$ and the resultant potential [here $R$ (distance from the symmetry axis) $= r\sin\theta$]:

$$\begin{aligned} &(1)\ \rho(\vec{r}) = \beta R, \quad V(r) = -\beta r^3/9; \\ &(2)\ \rho(\vec{r}) = \gamma R^2, \quad V(r) = -\gamma r^4/16. \end{aligned} \tag{8}$$

These incidentally illustrate immediately that the observed quadrupolar behavior of Mu is generally *not* measuring the standard $\langle r^2\rangle$ quadrupole moment of Mu. Using Eq. (7) and the wave function of Eq. (5), one can fit the parameters $\beta$ and $\gamma$ of our potentials to the observed frequencies. It is then interesting to estimate the additional quadrupole energy induced by the lattice potentials; this can be done using a closure estimate of $Q(V^2)$ matrix elements and in the above models is (10–20)% as large as that due to the *intrinic* $L = 2$ deformation.

It would be amusing to study experimentally Mu in quartz at low magnetic field, where $\Delta\nu$ is neither independent of $B$ nor proportional to $P_2(\cos\theta)$. With use of an apparatus now being constructed

at TRIUMF for regulation of fields as low as 1 mG with fixed orientation, these phenomena should be observable in detail via muonium-spin-rotation techniques. In particular, one should observe a purely quadrupole oscillation of $F = 1$ Mu in zero magnetic field. This should occur with the same frequency as the $\theta = \pi/2$ frequency splitting, namely 0.4 MHz, and is a unique signature of the interaction proposed.[11] We will also lower the temperature to look for axial asymmetry[7] if and when the Mu atom becomes "frozen" at a single site. If experimental equivalence between Mu and H can be established, then the above interpretation can be applied to H in $\alpha$-$SiO_2$ as well.

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[11]Since submission of this Letter, several runs at 30–70 G with $\vec{B} \parallel \hat{c}$ show that the quadrupolar effect described above always (for this orientation) acts to *increase* the quadratic Zeeman splitting, implying that $\Delta\nu_0$, as defined by Eq. (2), is *negative*, in accordance with the theoretical prediction of a positive electric quadrupole moment in the model potentials (8). Additional runs with *zero B field* (sample encased in Mumetal) and longitudinal counter geometry *confirm* the prediction of a single "quadrupole oscillation" frequency, measured to be $0.412 \pm 0.004$ MHz. The amplitude of this signal vanishes when $\hat{c}$ is parallel to the muon polarization, in accord with the assumption of axial symmetry in Eq. (2).

# Effect of Impurities on the Anomalous Transport Properties of $NbSe_3$

N. P. Ong, J. W. Brill, J. C. Eckert, and J. W. Savage[a]
*Department of Physics, University of Southern California, Los Angeles, California 90007*

and

S. K. Khanna and R. B. Somoano
*Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91103*

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Studies on the effect of charged (Ti) and uncharaged (Ta) impurities on the non-Ohmic behavior of and microwave absorption in $NbSe_3$ show that (1) the characteristic field $E_0$ increases as $c^2$ ($c$ = Ta concentration), in agreement with a recent calculation by Lee and Rice; (2) the microwave absorption is suppressed by impurities; and (3) charged impurities are strikingly more effective in supressing the anomalous properties. These conclusions provide very strong evidence for Fröhlich sliding-mode conductivity in the nominally pure compound.

The central question[1] in the study of charge-density-wave (CDW) or Peierls systems may very well be whether collective modes are significant in the conductivity in the CDW phase. The striking, anomalous transport properties[2,3] discovered in $NbSe_3$ below the two phase transitions at $T_1$ (142 K) and $T_2$ (58 K) have aroused much interest in this regard. Recent electron[4] and x-ray[5] diffraction measurements have confirmed superlattice formation at both $T_1$ and $T_2$, and it now appears certain that these anomalous properties are due to excitations in the CDW condensate. Below $T_1$ and $T_2$ $NbSe_3$ is non-Ohmic. It also shows a strong absorption mode at micro-

 