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Detection of EPR Transitions of Muonium in Quartz by Muon-Spin Rotation

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Magnetic resonance transitions of muonium in quartz have been detected by their effect on muon-spin-rotation frequency spectra. This technique can be used to observe EPR transitions which are not directly observable in the normal muon-spin-rotation spectrum. The coherence effects of an intense rf magnetic field on two strongly coupled spins are decribed theoretically and are found to explain the data in detail.

Positive-muon-spin-rotation experiments normally involve the study of the time history of the free precession of the muon spin by observation of the decay positrons.[1] For positive muons stopped in many insulators and semiconductors, an appreciable fraction of the muons bind an electron forming a muoniumlike state. In the case of quartz, a state very similar to muonium in vacuum is formed, having a reported hyperfine frequency of 4463 ± 300 MHz with a very slight anisotropy[2] (which can be ignored in the present work). Two frequency components are measured in the muonium time-differential muon-spin-rotation data, corresponding to the two allowed magnetic-dipole transitions within the $F=1$ triplet.

In this Letter we report for the first time the effect of EPR transitions on the muon-spin-rotation spectrum. We present muon-spin-rotation data taken while a single-crystal sample of quartz was in an intense rf magnetic field with a frequency near one of the two observed muonium frequencies. The resulting data give a very complete picture of the coherent response of two strongly coupled spins to an intense rf magnetic field—in effect, a double electron-muon resonance (DEMUR). The information obtained is similar to, but more detailed than, that obtained by various other double-resonance techniques (electron-nuclear double resonance, inequivalent-nuclear double resonance, electron double resonance, optically detected magnetic resonance).[3] In particular one observes the precessional component at the radio frequency and its two side bands, none of which can be probed in standard double-resonance experiments. A theoretical description of these effects is outlined and is found to be in excellent agreement with the data. Finally, it is argued that the DEMUR technique

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introduced here can be used to study EPR transitions which are not directly observable in the normal muon-spin-rotation spectrum.

Several magnetic resonance experiments on muons stopped in matter have been reported[4,5]; these experiments detected resonance via changes in the muon asymmetry in a longitudinal field. In contrast, our DEMUR experiment involves the effect of an rf field on the transverse muon-spin-rotation frequency spectrum. This difference is important for measurements in high fields where our calculations show that EPR transitions will affect the muon-spin-rotation frequency spectrum but not the muon-decay asymmetry in longitudinal field.

In this experiment, the technique of time-differential muon-spin rotation with a transverse static field of 125 G was used. A quartz single crystal (approximately 1-in. cube) was mounted inside a tightly wound three-turn coil, with its c axis parallel to the axis of the coil. The coil was part of an LC resonant circuit which was inductively driven by a 40-W broadband amplifier, whose input came from rf signal generator. Data were taken for several radio frequencies and rf amplitudes, for rf field parallel and perpendicular to the initial muon polarization (but always perpendicular to the static field), and for no rf field.

In a magnetic field of 125 G, the Zeeman splitting of the $F=1$ triplet is far less than the hyperfine splitting. Since our muon-spin-rotation experiment could not accurately measure frequencies higher than about 500 MHz, the only frequency components which are seen in the muon-spin-rotation spectrum are those corresponding to the $m_f=1$ to 0 and $m_f=0$ to -1 transitions within the $F=1$ triplet. These occur at approximately 167.2 and 180.5 MHz for a static applied field of 125 G.

The effect of an intense rf magnetic field is to split these two lines into several lines with frequencies and intensities which depend on both the frequency and the amplitude of the rf magnetic field. The muon-spin-rotation data were analyzed to obtain these frequency components and their intensities. Both Fourier analysis and multifrequency least-squares fits were employed with comparable results.

The results of such an analysis for three different experimental conditions are shown in Fig. 1. In Fig. 1(a), the power spectrum for muonium with no incident rf power shows the two lines, near 167.2 and 180.5 MHz. In Figs. 1(b) and 1(c), the resulting spectra for an applied rf field of approximately 3.2 G peak to peak are shown. In

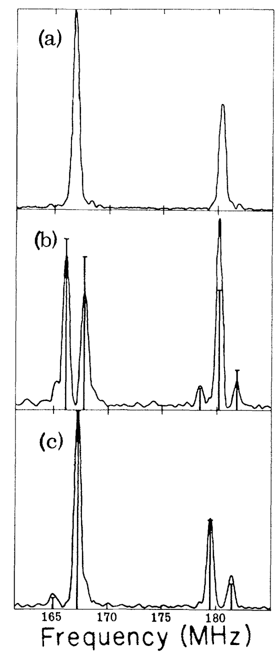

FIG. 1. Fourier-transform power spectra for muonium in quartz at room temperature and 124.85 G. The power spectra of 4×10^6-count time-differential muon-spin-rotation data taken over a 2-μsec interval by each of two position telescopes were combined to give the results in (b) and (c) while 2×10^6 counts per telescope were used for (a). In (a) no rf power was applied while in (b) and (c) the rf magnetic field had a peak amplitude of 1.6 G. In (b) the radio frequency was 180.279 MHz and the results are characteristic for the rf near the higher resonance frequency. In (c) the rf was 181.517 MHz, roughly 1 MHz above the higher resonance frequency. The vertical bars represent the calculated frequencies and powers.

Fig. 1(b) the radio frequency is near 180.5 MHz resulting in a strong line at the radio frequency flanked by two lines of nearly equal intensity, each with about half the amplitude of the strong line. In addition, the line at 167.2 MHz is split into two lines of comparable intensity. The splittings of the lower pair of lines and the upper three are all equal, to within experimental error, and the sum of the intensities of the two lower lines is about equal to that of the upper three. In Fig. 1(c), the rf is about 1 MHz above the 180.5-MHz resonance and the resultant changes in the line intensities and splittings can be seen. Again five lines result, one being at the radio frequency, but in this case the line above that at the rf is too weak to be observed.

Physically, the splitting of the muon-spin-rotation line near the rf is a modulation of the precessional frequency analogous to the effect of nutation for a single spin of $\frac{1}{2}$. The effect on the distant line (the "transfer effect") is more difficult to visualize, but it is similar to the splitting observed in ENDOR experiments with intense rf fields.[6] A quantitative description of this system can be obtained by solving the time-dependent Schrödinger equation, with neglect of all relaxation processes. The solutions[7] of the four coupled differential equations for the time-dependent amplitudes of the unperturbed (no rf) energy eigenstates were used to calculate the expectation values of the muon spin. In this calculation, the initial state has the muon completely polarized along the beam direction and a randomly oriented electron spin; the phase of the rf magnetic field at the time a muon stops is also taken to be random. In addition, all high-frequency contributions to the amplitudes are neglected. In the expressions below, the eigenstates are labeled from 1 to 4 going from highest to lowest energy, and the rf is ω. Only terms with the smaller of the frequencies $\omega-\omega_{23}$ and $\omega-\omega_{12}$ in the differential equations for the amplitudes have been retained ($\omega_{23}\equiv\omega_2-\omega_3$, etc.).[8] For $\omega\simeq\omega_{23}$, the muon polarization perpendicular to both the static magnetic field and the initial polarization direction is given approximately by

$$P=\frac{1}{4}\frac{s^2}{z^2+1}\sin\omega t+\frac{s^2}{8}\left[1+\frac{z}{(z+1)^{1/2}}\right]^2\sin[(\omega_{23}+2\omega_-)t]+\frac{s^2}{8}\left[1-\frac{z}{(z^2+1)^{1/2}}\right]^2\sin[(\omega_{23}+2\omega_+)t]$$
$$+\frac{c^2}{4}\left[1+\frac{z}{(z^2+1)^{1/2}}\right]\sin[(\omega_{12}-\omega_-)t]+\frac{c^2}{4}\left[1-\frac{z}{(z^2+1)^{1/2}}\right]\sin[(\omega_{12}-\omega_+)t],$$

where

$$\omega_\pm\equiv\tfrac{1}{2}[z\pm(z^2+1)^{1/2}]\omega_\alpha,\quad z\equiv(\omega-\omega_{23})/\omega_\alpha,$$
$$\omega_\alpha\equiv\tfrac{1}{2}(c\omega_0-s\omega_\mu),\quad \hbar\omega_0\equiv g\mu_B H_1,\quad \hbar\omega_\mu\equiv g_\mu\mu_\mu H_1.$$

The quantities s and c are the coefficients of the high-field basis states forming the energy eigenstates 2 and 4 ($c>s>0$), and H_1 is the amplitude of the linearly polarized rf field. For $\omega\simeq\omega_{12}$, the polarization is obtained by interchanging ω_{23} and ω_{12} as well as s and c. The results for $\vec{H}_1$ parallel and perpendicular to the initial muon polarization differ only in sign (the result shown is for parallel).

The splitting of the line farther from the rf is the most important, since it is this effect which generalizes to situations in which the EPR transition is not observable directly in the muon-spin-rotation data. As one can see from the equation, this transfer effect results in two lines with a splitting of $\Delta\omega=(z^2+1)^{1/2}\omega_\alpha$ and with the ratio of the intensity of the higher-frequency line to that of the lower given by $[(z^2+1)^{1/2}+z]/[z^2+1)^{1/2}-z]$. Only on resonance, $z=0$, are these two lines equally intense. The line close to the rf becomes a triplet, with one component at the driving frequency and the other two displaced above and below it by the same frequency splitting $\Delta\omega$ as in the transfer effect. Exactly on resonance, these three lines have intensities in the ratio 1:2:1. The relative amplitudes of the five lines are the most sensitive measure of z, the reduced displacement of the applied rf from resonance.

For all of the cases studied, the agreement between the experimental data and the theory given above is excellent. An example of this agreement is indicated in Fig. 1. The differences between theory and experiment are comparable to that expected from counting statistics. This agreement confirms the validity of the theoretical explanation and demonstrates conclusively that we have observed EPR by its effect on the muon-spin-rotation data.

An important conclusion from our results is that the resonance frequencies of EPR transitions can be measured using the DEMUR technique. In the present experiment an accuracy in the resonance frequency of about 5 parts in 10^4 was achieved, and higher accuracy should certainly be possible. At high fields and frequencies, or for other systems with a smaller hyperfine interaction, EPR transitions which do not show up as a component in the muon-spin-rotation frequency spectrum can be detected in close analogy to the transfer effect observed here. From such an observation one can obtain the electronic g tensor, as well as any structure characteristic of EPR spectra, such as nuclear hyperfine structure. This technique should thus prove useful in understanding the structure of defects in solids involving μ^+, such as "anomalous" muonium in silicon[9] and germanium,[10] and in studying the structure of muonium-containing free radicals.[11] Experiments of this nature are under way.

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Infinite Number of Order Parameters for Spin-Glasses

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This Letter shows that in the mean-field approximation spin-glasses must be described by an infinite number of order parameters in the framework of the replica theory.

From the theoretical point of view, spin-glasses are very important because they describe one of the most simple cases of amorphous material. A good framework to study spin-glasses is the replica theory[1]: One introduces an order parameter $Q_{\alpha,\beta}$ which is the limit, for n going to zero, of an $n \times n$ matrix, zero on the diagonal. In the mean-field approximation the statistical expectation value is different from zero only in the spin-glass phase, at zero magnetic external field. In the Sherrington-Kirkpatrick (S-K) model the mean-field approximation is exact in the thermodynamic limit.[2]

An intriguing feature of this scheme is the necessity of reaching the limit $n=0$ as analytic continuation in n from positive integer n. In the standard treatment of the S-K model one assumes that

$$Q_{\alpha,\beta}=q. \tag{1}$$

Here q is the Edwards-Anderson[1] order parameter and it is understood that Eq. (1) does not hold for $\alpha=\beta$ in which case $Q_{\alpha,\alpha}$ is identically zero.

This *Ansatz* [Eq. (1)] gives results at variance with the computer simulations[3] of the S-K model; moreover, one obtains a negative entropy at zero temperature, i.e., $S(0)=-0.17$ (the entropy of the model must be nonnegative by definition). It has been suggested that the wrong result is due to the fact that the true value of $Q_{\alpha,\beta}$ is not symmetric under permutations of the indices[4]: The parametrization Eq. (1) is not valid and the replica symmetry is broken. Various patterns of symmetry breaking have been proposed[5,6]; in a previous paper[7] it has been noticed that the pattern of symmetry breaking depends on a continuous variable which must be treated as a variational parameter.

If the matrix $Q_{\alpha,\beta}$ is parametrized as a function of three variables, quite good results have been obtained for the S-K model[7]: The agreement with the computer simulations is excellent and the zero-temperature entropy is quite small, with $S(0)=-0.01$. If we generalize this approach, the

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