with natural modes of oscillation of the fiber. The enhancement mechanism is identical to proposed local field enhancement mechanisms for SERS from metallic microstructures, where the analogous resonant modes are surface plasmon modes and the n, l values correspond to various multipolar plasmon resonances.

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Surface Relaxation of ^{3}He on Small Fluorocarbon Particles

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The nuclear magnetic polarization of ^{3}He on the surface of a fluorocarbon substrate is controlled by the polarization of the ^{19}F in the substrate. The apparent relaxation rates of the ^{3}He measure the coupling between the spin baths of the ^{3}He and the ^{19}F nuclei within the substrate.

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We have observed unusual nuclear relaxation and polarization phenomena in a fluorocarbon polymer in contact with films of ^{3}He. Our measurements show that the spin temperatures of the ^{3}He and the ^{19}F are held in close contact, most likely through the nuclear magnetic dipolar coupling at the interface.

In our experiments we packed a powder of fluorocarbon beads in a cylindrical coil form 4.8 mm in diameter and 9.5 mm high. We then measured the relaxation properties of the ^{19}F with various coverages of ^{3}He on the surface of the beads. The beads were approximately 0.2 μm in diameter and had a rather narrow size distribution. The polymer is quite similar to polytetrafluoroethylene (or Teflon) and is sold by Dupont under the trade name DLX-6000. Our measurements were conducted in the temperature range between 0.5 and 4 K. However, the temperature is apparently not an important variable in the phenomena we report here.

The most striking consequence of the coupling between the spins of ^{19}F and ^{3}He is illustrated in Fig. 1 where we demonstrate a type of spin pumping. The results shown are for some experiments with approximately one monlayer of ^{3}He. We found that the inversion of the spin population of the ^{19}F through the application of a π pulse at the ^{19}F resonance frequency also produced an inversion of the ^{3}He spin population. The figure shows the recovery of ^{19}F and ^{3}He magnetization in several different types of pulse experiments. Figure 1(a) shows the recovery of the ^{19}F magnetization following a π pulse at the ^{19}F resonance frequency. The recovery is approximately exponential and the characteristic time is about 10^3 sec. Part (b) shows the change in magnetization with time of the ^{3}He after the ^{19}F polarization has been inverted with a π pulse at the ^{19}F resonance frequency. The ^{3}He magnetization also becomes inverted and recovers to equilibrium with roughly the same time constant as the ^{19}F. Part (c) shows the recovery of the ^{3}He to equilibrium after the application of a $\pi/2$ pulse at the ^{3}He resonance frequency. The characteristic time in this case is only 200 msec. In other pulse experiments with the same coverage and in the same magnetic field, we found that quite generally the ^{3}He magnetization approaches a value determined by the ^{19}F polarization state in a characteristic time of 200 msec.

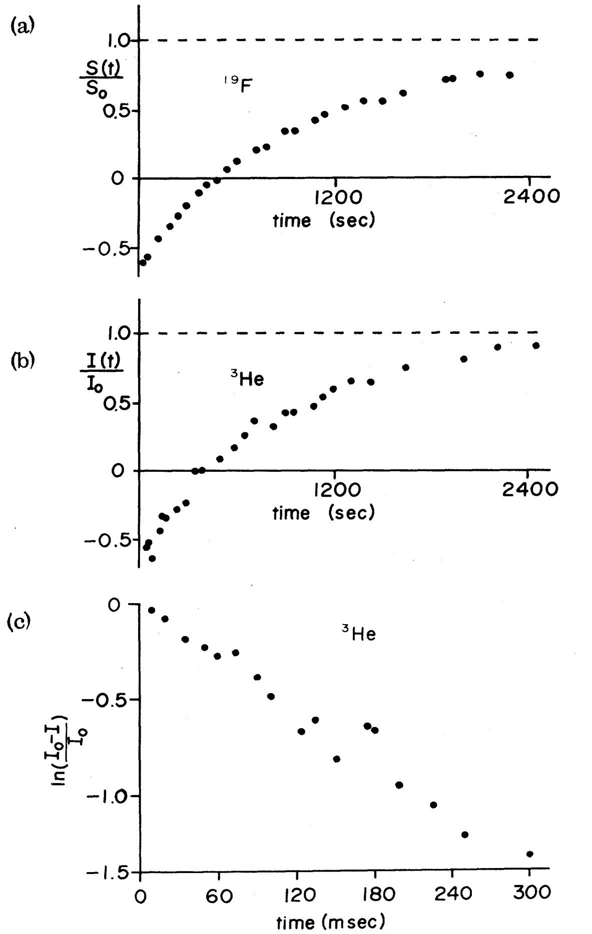

FIG. 1. Spin relaxation of ^{3}He and ^{19}F at 1.3 K and a field of 3.9 kG. (a) The recovery of ^{19}F following a spin-inversion pulse at the ^{19}F resonance frequency. S_0 is the equilibrium signal of ^{19}F measured at times longer than those shown. (The spin-inverting pulse is a little smaller than a π pulse.) (b) The ^{3}He polarization is also inverted by the radio frequency pulse applied at the ^{19}F frequency. The same pulse as that shown in (a) was applied to the ^{19}F. The data show the size of the ^{3}He signal measured at the ^{3}He resonance frequency at various times after the ^{19}F inversion. (c) The magnetization recovery of ^{3}He when measured in the usual manner. The ^{3}He spins were initially saturated with a $\pi/2$ pulse at the ^{3}He resonance and then the signal was sampled at various times shown. The data here are plotted in the customary logarithmic form. T_1 for ^{3}He deduced in this manner is 200 msec.

In a related experiment, we polarized the ^{19}F by raising the magnetic field to a large value, of order 10 kG, for several T_1 intervals of the ^{19}F, and then after we reduced the field to 4 kG, an enhanced ^{3}He magnetization persisted for times again characteristic of the T_1 of the ^{19}F spins.

We were also able to change the spin temperature of the ^{19}F through the repeated application of $\pi/2$ pulses to the ^{3}He. After the application of several hundred $\pi/2$ pulses at the ^{3}He resonant frequency with a repetition rate of 3 per sec, the ^{19}F magnetization reached an equilibrium size roughly half of that observed in the absence of the ^{3}He pulses. The application of a similar burst of rf pulses at nearly the same frequency, but not the ^{3}He resonant frequency, produced no effect on the ^{19}F signal, thus eliminating lattice heating as a possible explanation for this experiment.

The dominant relaxation mode for the ^{19}F nuclei is the dipolar interaction with the ^{3}He on the surface. In Fig. 2 the ^{19}F relaxation time T_1 at 1.3 K and with a Larmor frequency of 16 MHz is plotted as a function of the amount of ^{3}He admitted to the experimental cell. In the absence of ^{3}He the relaxation rate is an order of magnitude slower than that observed with the optimum coverage of ^{3}He. We assume that the peak rate occurs near

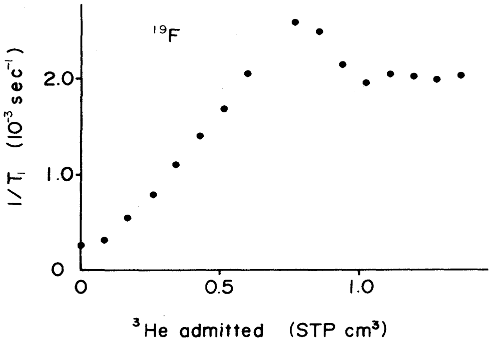

FIG. 2. Change in ^{19}F relaxation rate with ^{3}He coverage. The relaxation rate of the ^{19}F is enhanced when ^{3}He is added to the fluorocarbon spheres at low temperatures. With the addition of ^{3}He quantities larger than those shown in the figure, the ^{19}F relaxation rate remains unchanged.

a coverage of one monolayer. However, the 0.7 cm^3 (STP) of ^{3}He at the peak is about $\frac{2}{3}$ of a monolayer on the calculated geometrical surface area of the fluorocarbon spheres. Our sample is too small for a convenient surface-area calibration through the measurement of absorption isotherms with helium gas.

The results shown in Fig. 2 were initially somewhat surprising to us. In order to verify that the spins of the ^{3}He at the surface played the dominant role in the ^{19}F relaxation, we repeated the experiment with ^{4}He. We found that the addition of ^{4}He to the bare fluorocarbon surface had no effect upon the relaxation of the ^{19}F.

We can interpret the data shown in Figs. 1 and 2 with the following model. The ^{19}F nuclei relax through interaction with the ^{3}He at the surface; the ^{3}He in turn is coupled to the thermal bath through the motion of the atoms on the surface. We label the ^{19}F spins S and the ^{3}He spins I, the uncoupled relaxation times of the two spin species $T_1{}^S$ and $T_1{}^I$, and the time coupling the two spin baths as $T_1{}^{IS}$. The measured ^{19}F relaxation will be given by

$$\frac{1}{T_1{}^{S\,\mathrm{meas}}} = \frac{1}{T_1{}^S} + \frac{1}{T_1{}^{\mathrm{surf}}},$$

with $T_1{}^{\mathrm{surf}} = T^{\mathrm{spin\ diffusion}} + (N_S/N_I)(T_1{}^{IS} + T_1{}^I)$. The time for surface relaxation of ^{19}F thus includes the series processes for the diffusion of the spin excitation to the surface, the coupling of the excitation across the interface, and finally the intrinsic relaxation time of the ^{3}He surface atoms where each of the N_I atoms shares the burden of relaxing N_S/N_I ^{19}F spins.

The spin diffusion constant for the dipolar interaction between ^{19}F spins is of order $a^2\omega_d$, where a is the distance between the ^{19}F atoms, and $\omega_d \simeq (\gamma_S{}^2\hbar/a^3)$ is the rate of dipolar spin flips between ^{19}F neighbors, with γ_S the gyromagnetic ratio of the ^{19}F nuclei. For a sphere of radius r the diffusion relaxation time is thus of order $T^{\mathrm{s.d.}} \simeq r^2/D = r^2 a/\gamma_S{}^2\hbar$. In our case with $r = 0.1$ μm, $a = 3$ Å, and $\gamma_S = 2.5\times10^4$, we expect this time to be of order 5 sec. Gates and Potter[1] have studied the spin diffusion of ^{19}F in small Teflon particles with O_2 impurities on the surface for rapid relaxation. In our case the observed relaxation times of the ^{19}F are much longer than the diffusion time and so the "bottleneck" occurs in the surface process. Even with this surface bottleneck, the surface process is faster than that available for the bulk so that in the presence of the ^{3}He, $T_1(^{19}\mathrm{F}) = (N_S/N_I)(T_1{}^{IS} + T_1{}^I)$.

The experiments producing the spin inversion of ^{3}He after the π pulse on the ^{19}F spins show that the ^{3}He is more strongly coupled to the ^{19}F spin bath than to the thermal reservoir of its own lattice motion. This coupling time constant is of order 200 msec, and we identify it with the parameter $T_1{}^{IS}$. The time constant coupling the ^{3}He to the lattice might thus be[2]

$$T_1{}^I = (N_I/N_S)T_1{}^{S\,\mathrm{meas}} - T_1{}^{IS} \simeq (N_I/N_S)T_1{}^{S\,\mathrm{meas}} \simeq 10\ \mathrm{sec},$$

since $N_I/N_S \simeq 10^{-2}$.

The spectral efficiency of the interaction between the ^{19}F nuclei and the ^{3}He remains a perplexing problem. The field dependence of the relaxation rate might be expected to have the usual form for the dipole interaction[3]:

$$\frac{1}{T_1{}^{IS}} \simeq \frac{\gamma_I{}^2\gamma_S{}^2\hbar^2}{a_{IS}{}^6}\left(\frac{\tau}{1 + H_0{}^2(\gamma_I - \gamma_S)^2\tau^2}\right),$$

where a_{IS} is the distance between the I and S spins, H_0 is the applied magnetic field, and τ is an atomic collision frequency. In the range of magnetic fields between 0.8 and 8 kG, we measure T_1 values for both ^{19}F and ^{3}He which increase roughly linearly with the magnetic field. Evidently the usual assumption of an exponential correlation function of the form $\exp(-t/\tau)$ is invalid.

The times we have measured for the ^{3}He relaxation are comparable to those seen in other studies of ^{3}He on a variety of surfaces such as glass and graphite.[4] The linear field dependence of T_1 has also been observed on these other substrates. The question arises of whether the results of other experiments have also been influenced by possible nuclear dipole coupling to the substrate. It has usually been assumed that the removal of paramagnetic oxygen impurities on the surface is sufficient to ensure that intrinsic relaxation processes are observed on the surface.

The results of the present experiment also bear upon the interpretation of studies in bulk liquid ^{3}He. The relaxation of ^{3}He in bulk liquid is usually dominated by the surface processes at low temperatures. Models of surface relaxation of liquid ^{3}He should thus include the strong interaction with nuclear magnetic moments in surfaces contacting the liquid. Most models of surface relaxation to date have considered only electronic or ionic moments in the substrate.[5,6]

Also to the extent that these results are found on other substrates, the interpretation of experiments measuring the "anomalous surface magnetization" of liquid ^{3}He may be changed. In a number of experiments a Curie-Weiss law has been measured for the ^{3}He in the surface layer (or surface layers).[7-10] Our results suggest that the polarization of the surface layer would be determined by the competition between the nuclear magnetic dipole interaction of the ^{3}He with nuclei in the underlying substrate and the interaction with the ^{3}He atoms in the bulk liquid. The temperature dependence of the surface ^{3}He magnetic susceptibility should be governed by the polarization of the nuclei in the underlying surface and the relative strengths of the thermal coupling of the surface ^{3}He spin bath with the bulk liquid and with the substrate nuclei. The intrinsic tendency of the surface layer toward any type of magnetic order may well be masked by the surface interactions.

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[2] One may be tempted to identify this time with the intrinsic relaxation time which ^{3}He might have had if there were no nuclear moments or oxygen impurities within the substrate. This is not necessarily the case because the dipolar interaction contains terms coupling I^z with $S^\pm$ and S^z with $I^\pm$. Ordinarily these terms which serve to change the state of the S population without changing the I spins are just as important as the cross terms coupling $S^\pm$ with $I^\mp$. Curiously, in the case studied here this is not the case. The success of our spin pumping experiments depends upon the existence of a much stronger coupling between the two spin baths than the coupling of the ^{3}He spin bath to the lattice.

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