

## Dynamic nuclear polarization of liquid $^3\text{He}$ in powdered charcoal

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By inducing electronic spin flips in a powdered sucrose charcoal immersed in liquid  $^3\text{He}$ , we have produced a steady-state enhancement of the nuclear polarization in the liquid. In a magnetic field of 182 G and at a temperature of 1.8 K, the maximum positively enhanced polarization was 18% greater than the equilibrium value. Magnetic relaxation times of the liquid are unaffected by the enhancement. The results demonstrate the existence of a magnetic coupling between the liquid  $^3\text{He}$  and the charcoal substrate, similar to that found by other investigators for fluorocarbon substrates.

Interactions between liquid  $^3\text{He}$  and solid samples with large specific surface areas have been the subject of many studies.<sup>1-7</sup> Recent theoretical work<sup>6,7</sup> suggests that magnetic interactions between the  $^3\text{He}$  and spins within solids in contact with the helium can be used to dynamically polarize<sup>8,9</sup> the helium by saturating electron-spin-resonance (ESR) transitions in the solid. The first experimental dynamic polarization of  $^3\text{He}$  (in thin films and in bulk liquid) was produced by pumping ESR transitions in a fluorocarbon powder in  $^3\text{He}$ .<sup>4,5</sup> Such dynamic polarization experiments provide a powerful probe of the magnetic interactions between  $^3\text{He}$  and solids. In this Rapid Communication, we report the dynamic polarization enhancement of liquid using a solid other than the fluorocarbon powder.

We chose to use a sucrose charcoal because it is easily prepared, it has a large specific surface area, and it can be produced to have an easily saturated ESR resonance<sup>10,11</sup> which has been used in previous experimental work to dynamically polarize  $^1\text{H}$  nuclei within and adsorbed on the char.<sup>12-14</sup> Our sample was prepared from reagent grade sucrose, which was heated under flowing argon in a glass tube in an oven. The temperature was gradually raised to 425°C over an eight hour period, kept at the value for sixteen hours, then slowly reduced by turning off the oven. While cooling, the sample tube was evacuated, but the cooled sample was exposed to air for grinding and packing into the experimental cell.

By calibrating against a sample of diphenylpicrylhydrazyl (DPPH), we find that the sample contains roughly  $10^{19}$  spins/cm<sup>3</sup> when measured in air at room temperature, but after being kept in vacuum for 48 h, the spin density quadruples. This sensitivity to oxygen adsorption has been observed in previous work,<sup>10,11,13</sup> and seems to indicate that the paramagnetic centers are easily accessible from the surfaces. Elemental analyses of similar charcoals<sup>10,13</sup> indicate that hydrogen accounts for about 5% of the sample by weight. With the measured average density of our sample, and a packing fraction estimated to be near 50%, the number of hydrogen spins in the sample is about four times greater than the number of  $^3\text{He}$  spins in the liquid surrounding it when the experimental cell is at the operating temperature and pressure.

The ESR resonator (see Fig. 1), which is of the "slotted tube" type,<sup>15</sup> has a resonant frequency of 509.6 MHz, and an unloaded  $Q$  at low temperatures of 800; it produces a UHF field amplitude ( $2H_1$ ) of roughly 0.5 G when dissipating 1 mW. A high-homogeneity, air-core solenoid outside

the Dewar provided the static field. Using standard pulsed nuclear magnetic resonance (NMR) on the liquid  $^3\text{He}$ , we observed free-induction-decay times of 40 msec. To determine the nuclear magnetization, we measured the initial amplitude of the free-induction-decay signal. All of the measurements were made with the  $^3\text{He}$  at a temperature of 1.8 K and at a pressure of 330 torr.

The polarization enhancement was determined by comparing the NMR amplitude  $M$  when the UHF field was on with the NMR amplitude  $M_0$  when the ESR field was off. The enhancement, defined as  $\Delta = (M - M_0)/M_0$ , is plotted as a function of the static field in Fig. 2. The maximum positive enhancement was 18%. The enhancement was zero when the static magnetic field was at the center of the ESR resonance, and negative when the static field was below the resonance value, indicating that the dynamic polarization occurs through dipolar coupling between electronic and nuclear spins.<sup>9</sup> The field separation between the maximum positive and negative enhancement points is approximately the electron linewidth, as expected for a dynamic polarization experiment where the ESR half-width is greater than the nuclear Larmor frequency. For the charcoal sample and resonator used in these experiments, the ESR is centered at 181.7 G with a full linewidth at half maximum of 6.0 G at 1.8 K.

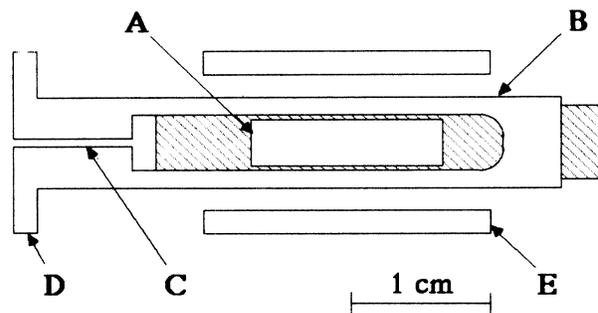


FIG. 1. Simplified diagram of the double resonance cell. The charcoal and  $^3\text{He}$  (region A) are contained in a nylon tube (cross hatched) which is inside the copper slotted-tube resonator (B). The slotted tube has an inner diameter of 0.51 cm, and produces a UHF magnetic field normal to the page. The spacing of the capacitive section of the resonator (C) is shown enlarged for clarity. Small capacitors attached to plates (D) on the resonator couple it to a balanced drive. The NMR coil (E) produces an RF magnetic field along the axis of the slotted tube (horizontal in the diagram), and an external solenoid produces a vertical static magnetic field.

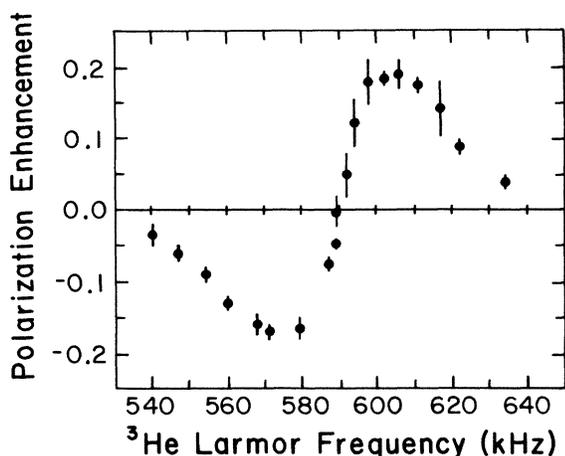


FIG. 2. The steady-state enhancement of the nuclear polarization in liquid  $^3\text{He}$  as a function of applied field, specified as the  $^3\text{He}$  Larmor frequency, in kHz. The center of the ESR line is at 589.3 kHz.

To obtain information about the dynamics of the enhancement process, we also measured the relaxation rates for the  $^3\text{He}$  magnetization. The longitudinal relaxation time  $T_1$  (characterizing the time it takes the  $^3\text{He}$  nuclear magnetization to return to its steady-state value after a tipping pulse) was  $1.02 \pm 0.03$  sec at the center of the ESR line. Within the accuracy of our measurements, our  $T_1$  values were unaffected by the UHF field at all static fields, including those of the center of the ESR and those producing maximum positive and negative enhancements. The dynamic polarization process was comparably fast: When the ESR field was first turned on, the approach of the nuclear magnetization to its new enhanced value was exponential, with a time constant of  $1.5 \pm 0.1$  sec.

The dependence of the polarization enhancement on the UHF power level was also measured. All of the measurements described in preceding paragraphs were made while dissipating about  $100 \mu\text{W}$  in the ESR resonator. For lower power levels, we find that the steady-state enhancement depends nonlinearly on the applied power. Using a power-law fit for the enhancement as a function of applied power, the best exponent is 0.3. With the small power dissipation in our cell, and the weak dependence of enhancement on the UHF power, experiments at considerably lower temperatures should be feasible.

Our findings that the relaxation time of  $^3\text{He}$  is independent of the dynamic polarization can be compared with relaxation measurements on  $^3\text{He}$  in contact with the fluorocarbon powder. Friedman, Gramila, and Richardson<sup>3</sup> found that saturating the  $^{19}\text{F}$  NMR in the powder reduced the  $^3\text{He}$  magnetization, but did not affect the  $^3\text{He}$   $T_1$ . In both experiments the liquid magnetization relaxes to a steady-state value in equilibrium with the substrate, which may or may not be in thermal equilibrium. The liquid's steady-state magnetization may be changed by destroying or flipping magnetization in the substrate, but the rate at which the liquid magnetization approaches equilibrium with the substrate is unchanged.

An interesting difference between our experimental results and those obtained by Schuhl, Maegawa, Meisel, and Chappellier<sup>5</sup> in their experiments dynamically polarizing  $^3\text{He}$  in a packed fluorocarbon powder, is in the enhancement

rates. Their time constant,  $T_e$ , for enhancing the  $^3\text{He}$  polarization was always at least ten times longer than the  $^3\text{He}$   $T_1$ , but in our experiments  $T_e$  was only 1.5 times larger than the  $^3\text{He}$   $T_1$ . The ratio of  $T_e$  to the  $T_1$  can provide information about the mechanism by which the  $^3\text{He}$  is dynamically polarized. Schuhl *et al.*<sup>5</sup> can identify their relatively long  $^3\text{He}$  enhancement times with the enhancement time of the  $^{19}\text{F}$  in the fluorocarbon powder. This leads them to propose a model in which the  $^{19}\text{F}$  in the powder is dynamically polarized, and its magnetization is transferred to the liquid  $^3\text{He}$ , so that the dynamic polarization for the  $^3\text{He}$  involves an indirect mechanism. It may be that the same indirect mechanism occurs in the charcoal we used, with  $^1\text{H}$  being dynamically polarized and then interacting with the  $^3\text{He}$ . However, we were not able to measure  $T_1$  for the  $^1\text{H}$ ,<sup>16</sup> so we cannot confirm the indirect mechanism. In a different model, in which the  $^3\text{He}$  is polarized by its magnetic interaction with the electronic spins of a solid surface, the time constant and magnitude of the enhancement are determined by competition between the dynamic polarization and  $T_1$  processes,<sup>7</sup> so a larger steady-state enhancement implies a faster initial rate of polarization. Our result that  $T_e/T_1 \approx 1.5$  may be consistent with this direct type of mechanism, but it is also consistent with a mechanism having an intermediate step of dynamic polarization in the solid, such as that in Ref. 5.

It is reasonable to assume that dynamic polarization of liquid  $^3\text{He}$  can be achieved by contact with a wide variety of solids; our experiments with the above described charcoal sample were our first attempt to observe the dynamic polarization of liquid  $^3\text{He}$ . To our knowledge, however,  $^3\text{He}$  has so far been dynamically polarized only in this charcoal and in the fluorocarbon powder. In spite of similar magnitudes of enhancement obtained in the two different samples, one cannot conclude that the efficiency of the dynamic polarization process is roughly equal for the two materials, since the conditions of the two experiments were very different. Schuhl *et al.*<sup>5</sup> used much lower temperatures, which affects the properties of the liquid  $^3\text{He}$ , and they did not use a resonator for exciting the ESR, so the applied UHF field strengths were probably lower than for our case. Further experiments will be necessary to understand and optimize the dynamic polarization of liquid  $^3\text{He}$  through its contact with a solid.

Our main result, that liquid  $^3\text{He}$  can be dynamically polarized by pumping ESR transitions in a powdered charcoal immersed in the liquid, proves the existence of a magnetic interaction between the electronic moments in the solid and the nuclear moments in the liquid, but the experiments do not provide much information about the nature of that interaction. The interaction may involve nuclear moments in the solid, as suggested in Ref. 5 for the polarization of liquid  $^3\text{He}$  using a fluorocarbon powder, but simple dipole-dipole interactions between the electrons and the  $^3\text{He}$  cannot be ruled out. To learn more about those interactions, future studies should include measurements of the nuclear polarization within a variety of substrates immersed in liquid  $^3\text{He}$ .

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- <sup>16</sup>Our apparatus has a plastic sample holder. The maximum static field in the magnet is so low that we would not be able to resolve the resonances of  $^1\text{H}$  or  $^{19}\text{F}$  in the holder from  $^1\text{H}$  in the charcoal. Furthermore, the  $^2\text{H}$  in the charcoal should have a small  $T_2$ , so that the free-induction decay would be too fast for our present electronics.