Production of Enhanced Liquid ^{3}He Magnetization by Dynamic Nuclear Polarization

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(Received 12 February 1985)

The first steady-state enhanced nuclear polarization of liquid ^{3}He has been produced by dynamic nuclear polarization. The ^{3}He is in contact with a high–surface-area fluorocarbon substrate containing electronic paramagnetic centers. Slightly off-resonant irradiation of the electronic spins cools the ^{19}F nuclear spins in the substrate through a dipolar interaction. The ^{19}F subsequently transfers magnetization to the ^{3}He through a ^{19}F-^{3}He interaction. Our results are in good agreement with recent models which explain this coupling.

PACS numbers: 76.70.Ey, 67.50.Dg, 76.60.Es

As a result of widespread interest in polarized systems, liquid ^{3}He has been the focus of recent experimental and theoretical investigations.[1] Significant polarization of pure liquid ^{3}He is not possible by "brute force," high magnetic field and low temperature, because the magnetization is limited by Fermi statistics and presently available magnets. On the other hand, polarization up to approximately 25% has been obtained for a period of several minutes by rapid melting of a highly polarized solid[2-5]; however, these experiments are inherently nonequilibrium in nature. Alternatively, dynamic nuclear polarization (DNP), which has been extensively employed to obtain polarized targets in nuclear physics, offers the possibility of achieving enhanced steady-state polarizations.[6]

The method of DNP has been successfully used to enhance the polarization of a ^{3}He monolayer adsorbed on fluorocarbon beads containing electronic paramagnetic centers.[7] The processes of this monolayer experiment involved polarization transfer from the electronic reservoir to the ^{19}F nuclei which then exchanged magnetization with the ^{3}He. This magnetization-exchange process was mediated by coupling between the ^{3}He "solid-like" surface layer and the ^{19}F of the substrate.[8-12] Chapellier[13] has suggested that if an exchange of magnetization rather than temperature occurs at the interface between the liquid ^{3}He and the solidlike surface layer, the magnetization enhancement experienced at the surface will be transmitted to the liquid. In this Letter, we have used the DNP to produce the first steady-state magnetization enhancement of the Fermi liquid ^{3}He.

The principle of DNP has been extensively reviewed,[6] but briefly this method is based on the existence of a dipolar interaction between the electronic and nuclear spins of the system. In the simplest picture, DNP may be viewed as a microwave cooling of the electronic spin-spin reservoir which subsequently reduces the spin temperature of the surrounding nuclei. This may be accomplished by external microwave irradiation at a frequency ν which differs slightly from the electronic Larmor frequency ν_e, i.e., $\nu = \nu_e + \Delta$. This irradiation may produce an increase ($\Delta < 0$) or decrease ($\Delta > 0$) of the nuclear polarization relative to its equilibrium value. When the electronic linewidth is larger than the nuclear frequency ν_n, the enhancement factor of the nuclear magnetization, α, is given [Eq. (5.9) of Ref. 6] by

$$\alpha - 1 = \frac{(\nu_e/\Delta)(\Delta^2/D^2)(1+f)^{-1}}{A + (\Delta^2/D^2)(1+f)^{-1}}, \tag{1}$$

where $A = (1 + WT_{1,Z})/WT_{1,D}$ depends on the dipolar, $T_{1,D}$, and Zeeman, $T_{1,Z}$, relaxation times of the electrons and on the electronic transition rate W; f is a magnetization leakage factor, i.e., the ratio between the rate of the nuclear relaxation due to processes other than coupling with the electrons and the nuclear relaxation rate due to the coupling with the electrons; and D is equal to the electronic linewidth within a multiplicative factor close to unity depending on the shape of this line. The maximum enhancement predicted by Eq. (1) is

$$\alpha_{\max} = 1 + (\nu_c/2\Delta_m); \quad \Delta_m^2 = AD^2(1+f). \tag{2}$$

The details of the experimental cell are schematically shown in Fig. 1. Thermal contact between the cell and the mixing chamber of the dilution refrigerator was made through two pieces of silver. The 1-mm-diam Ag wire of the cell (Fig. 1) was connected to the end of a 6-mm-Ag rod whose other end was embedded in a Ag sinter disk located in the mixing chamber. A melting curve thermometer[14] (MCT) was also thermally anchored to the 6-mm-Ag rod. Above 30 mK, the temperature measured by the MCT was in good agreement with the temperature extracted from the ^{19}F nuclear susceptibility, when a Curie law was assumed.[9] Because of the increasing inefficiency of the thermal path at lower temperatures, the agreement between the two thermometers deteriorated, and the temperature was measured from the ^{19}F system.

The substrate consists of fluorocarbon polymer beads[15] which were pressed into a plastic[16] cell (Fig. 1) with a packing fraction of approximately 0.7. These spheres have a diameter of 2000 Å which ensures a rapid ^{19}F magnetic diffusion between the interior and the surface. A large concentration ($\sim 2.6\times10^{18}$/cm^3) of

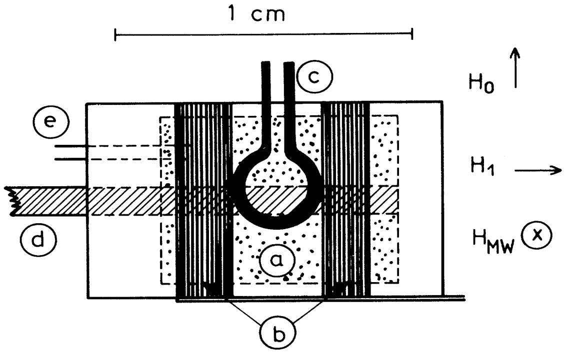

FIG. 1. A schematic drawing of the experimental plastic cell showing (a) the location of the fluorocarbon beads; (b) a 2×80-turn Helmholtz NMR coil providing the H_1 field; (c) the one-turn microwave coil providing the H_{mw} field; (d) a 1-mm-diam Ag wire providing thermal contact with a 6-mm-diam Ag rod connected to the mixing chamber; and (e) a filling capillary for ^{3}He. The cell is located in a high homogeneous superconducting solenoid providing the H_0 field.

electronic paramagnetic centers is known to exist in this substrate.[7] With use of an experimental configuration which consisted of substituting the coils labeled (b) and (c) in Fig. 1 with a suitable EPR coil, the electronic absorption line of our sample was measured in 300 G at 100 mK. The width of the signal ΔH was observed to be 12 G. For the DNP experiments, microwave irradiation was provided by a single-turn, untuned coil, Fig. 1, which was located outside of the cell and anchored to the 1.4-K heat shield.

The magnetization measurements were performed by means of conventional continuous-wave NMR techniques. The majority of the work reported in this Letter was conducted in a field of approximately 300 G, which corresponds to ^{3}He and electronic resonance frequencies of 970 kHz and 840 MHz, respectively. This field was chosen as a compromise between two experimental restrictions. Firstly, in low field the nuclear absorption line of the ^{1}H in the plastic cell overlaps the ^{19}F signal. Since both spectra have homogeneous widths of approximately 10 G, a minimum field of 300 G is necessary to separate the two lines clearly (Fig. 2). Secondly, the coaxial cable and excitation coil used for the microwave irradiation are rather inefficient for transmitting frequencies greater than 1 GHz. Consequently, an extension of our experiments to higher microwave frequency would require better microwave transmission to a tuned microwave cavity.

Our investigations involved the ^{19}F spheres immersed in pure liquid ^{3}He (<10 ppm ^{4}He). Consistent with the results of other workers[9,11] the relaxation time of the ^{19}F, $T_{1,\mathrm{F}}$, was measured to be 15 s at 20 mK while the recovery time of the ^{3}He, $T_{1,\mathrm{He}}$, was less than 1 s. Under these conditions, we were able to increase or decrease the magnetization of both ^{19}F and

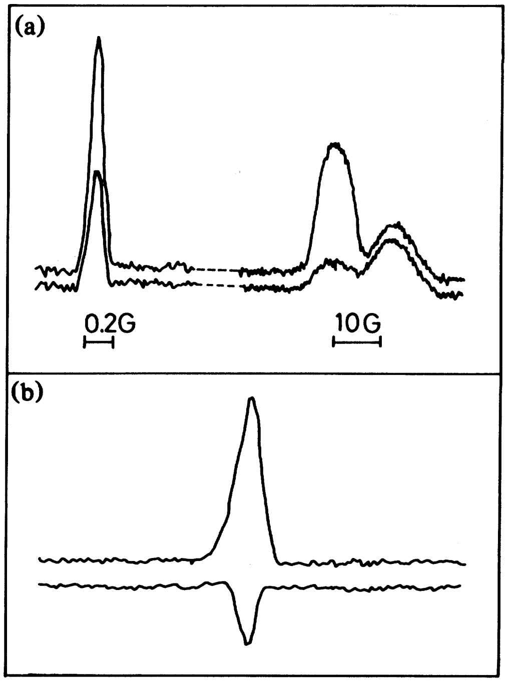

FIG. 2. Typical results of positive (a) and negative (b) DNP are shown when 0.6 layer of ^{4}He is present on the fluorocarbon-^{3}He interface. The NMR frequency is 970 kHz. In (a), the cw-NMR signals of the three nucler species ^{3}He, ^{19}F, and ^{1}H, left to right, are shown, at $T = 250$ mK before microwave irradiation (lower curve) and after 6 min of irradiation at $\Delta = -20$ MHz (upper curve). The enhancement factors are $\alpha_{\mathrm{F}} = 4.6$ and $\alpha_{\mathrm{He}} = 2.0$. In (b), only the ^{3}He signal is shown at $T = 150$ mK, before irradiation (upper curve) and after irradiation at $\Delta = 20$ MHz (lower curve).

^{3}He when an appropriate Δ was chosen. In a typical experiment, for example, with $\Delta = -20$ MHz and $T = 90$ mK, maximum ^{19}F and ^{3}He enhancements of $\alpha_{\mathrm{F}} = 1.30$ and $\alpha_{\mathrm{He}} = 1.25$ were obtained after a microwave irradiation time T_{mw} of approximately 10 s. All of our results of the enhancement factors, $\alpha_{\mathrm{F}} > \alpha_{\mathrm{He}}$, and of the time constants, $T_{1,\mathrm{F}} \gtrsim T_{\mathrm{mw}} \gg T_{1,\mathrm{He}}$, are consistent with the picture where the important DNP mechanism is electron-^{19}F rather than electron-^{3}He spin-polarization transfer. After being polarized, the ^{19}F rapidly transmit their polarization to the ^{3}He through the coupling between the two nuclear spin baths.[8-12] In order to improve the observed enhancements, Eq. (1) suggests that the terms A and f must be decreased, and this may be accomplished by an increase of the microwave power and/or by an increase of $T_{1,\mathrm{F}}$.[6] An immediate increase in the microwave power was not possible in our experiments because of the constraints previously discussed and because of the presence of eddy-current heating in the Ag wire. On the other hand, it is well established that the presence of ^{4}He on the surface of the beads slows down the ^{19}F relaxation.[17,18] This increase of $T_{1,\mathrm{F}}$ is a consequence of a reduction in the ^{19}F-^{3}He coupling strength and a lengthening of the ^{3}He Zeeman-lattice relaxation time, T_Z. If models[11–19] which suggest that these two factors involve exchange in the surface layer are correct, one may reasonably infer that the two mechanisms may be comparably affected by low ^{4}He coverages. Therefore, larger α_F and α_He values may be possible by the introduction of small amounts (less than 1 atomic layer) of ^{4}He since $T_{1,\mathrm{F}}$ would increase and the ^{19}F-^{3}He coupling rate would remain comparable to T_Z^{-1}.

With this motivation, the DNP experiments were performed with 0.6 ± 0.1 layers of ^{4}He on the surface of the beads.[20] With this condition, $T_{1,\mathrm{F}}$ lengthened to 10 min while $T_{1,\mathrm{He}}$ became 10 s at $T = 50$ mK. Nevertheless, the ^{19}F-^{3}He coupling remained rather efficient since total saturation of the ^{19}F magnetization caused the ^{3}He signal to drop to 70% (instead of 30% for pure ^{3}He) of its equilibrium value in a time close to $T_{1,\mathrm{He}}$. Figure 2 shows typical DNP experimental results obtained at $T = 250$ mK when 0.6 layer of ^{4}He covers the substrate. The positive enhancement factors of $\alpha_\mathrm{F} = 4.6$ and $\alpha_\mathrm{He} = 2.0$ are significantly larger than the results obtained in the pure-^{3}He experiments. During irradiation, the ^{19}F and ^{3}He magnetizations approached their new steady-state equilibrium values with a time constant equal to 2.6 min. In addition, the enhanced magnetization of the ^{3}He in Fig. 2(a) is 1.5 times larger than the equilibrium value at $T = 0$. This result was also observed at $T = 50$ mK where the Fermi liquid ^{3}He is almost totally degenerate. The observation of ^{3}He polarization larger than the $T = 0$ equilibrium value is compatible only with a magnetization exchange, rather than temperature exchange, between the solidlike surface layer and the liquid. Moreover, we have observed the ^{19}F-^{3}He coupling ratio $(\alpha_\mathrm{He} - 1)/\,(\alpha_\mathrm{F} - 1)$ to be equal for both saturation and DNP investigations. This result clearly supports the magnetization-exchange hypothesis and is further evidence that the dominant electronic-spin-polarization transfer is electron-^{19}F rather than electron-^{3}He transfer. Furthermore, our ability to produce positive and negative polarization enhancements (Fig. 2) provides unambiguous evidence of the DNP process in our experiments rather than an Overhauser-type effect.[21]

When additional ^{4}He is added so that more than 2.0 layers cover the spheres, the ^{19}F-^{3}He coupling is severed, and $T_{1,\mathrm{F}}$ is maximized. With these conditions we measured $\alpha_{\max,\mathrm{F}} = 6.0$ while α_He remained unity. In order to compare our results with the predictions of Eq. (2), we have measured α_F as a function of H_0 and have deduced that $\Delta_m = 30$ MHz. With this value of Δ_m, Eq. (2) gives $\alpha_{\max,\mathrm{F}} = 14.5$. The difference between the experimental and the predicted values of $\alpha_{\max,\mathrm{F}}$ can be attributed to an inhomogeneity of our microwave irradiation field.

Let us discuss briefly how these results may be improved. Firstly, one should attempt to improve the enhancement of the polarization of substrate nuclei, α_n. This improvement could be achieved through the use of electronic centers with narrow linewidths and a better microwave device. At this point, it is important to realize that a decrease of the temperature T much below the Fermi temperature will not permit an increase of the maximal liquid ^{3}He polarization. By lowering T one should obtain a higher polarization P_n of the nuclei in the substrate since its equilibrium value P_n^0 will increase. However, the maximal liquid-^{3}He polarization P_He is given by $P_\mathrm{He} = P_\mathrm{He}^0 \times (P_n/P_n^0)$, where P_He^0 is the liquid equilibrium polarization, and hence, does not depend on T as long as α_n may be considered independent of T. Secondly, the best balance, for the solidlike layer, between the spin-lattice relaxation (which loses polarization) and the coupling to the substrate nuclei should be established by a more complete knowledge of the magnetic and thermodynamic properties of ^{4}He-^{3}He mixed surface layer. Alternatively, the coupling between the substrate nuclei and the ^{3}He may be improved directly by use of materials which offer the possibility of a Zeeman crossing between the two nuclear spin systems when the external parameters are varied, for example, rotation of the magnetic field H_0 for anisotropic nuclear magnetic systems,[22,23] or the choice of an appropriate value of H_0 for nuclei with quadrupolar interaction. Finally, it should be noted that the DNP method is not limited to confined ^{3}He. One may polarize the bulk liquid to a depth of approximately $l = (D_l \times T_1)^{1/2}$, where D_l and T_1 are the bulk liquid diffusion constant and relaxation time, respectively. This distance l increases as T^{-2} at low T is several millimeters at 50 mK.

In conclusion, although achieving modest enhancements, our experiments have demonstrated the possibility of dynamic nuclear polarization of the Fermi liquid ^{3}He. We have produced steady-state liquid ^{3}He with positive and negative polarization enhancements and with magnetizations larger than the $T = 0$ equilibrium value. These results follow from the original idea of Chapellier[13] and are different from another recent proposal.[21] Our observations also provide clear evidence of a magnetization-exchange process between the solidlike surface layer and the liquid.

We have benefitted from stimulating discussions with R. C. Richardson and P. C. Hammel and thank them for communicating their work prior to publication. We thank H. Alloul and R. C. Lacoe for a critical reading of the manuscript. This work was performed by Direction des Recherches, Etudes, et Techniques under Contract No. DRET 81/431/. One of us

(M.W.M.) acknowledges the receipt of a 1984/1985 North Atlantic Treaty Organization Postdoctoral Fellowship administered by the National Science Foundation. Laboratoire de Physique des Solides is laboratoire No. 2 associé au Centre National de la Recherche Scientifique.

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