

Nuclear Polarization Enhancement by Distillation of Liquid ^3He - ^4He Solutions

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A closed-cycle distillation column was operated on a helium-3–helium-4 mixture in an attempt to “separate” the two nuclear-spin states of helium-3. For the atoms in the dilute phase, a steady-state polarization 3.5 times larger than that of the equilibrium was obtained; possible ways to improve this result are discussed.

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Obtaining highly polarized liquid helium-3 has been an important issue for many years: Nuclear polarization can affect transport properties [1], as well as equilibrium characteristics, for example, the liquid-gas equilibrium diagram [2]. Liquid helium-3 is a Fermi system with a finite magnetic susceptibility at low temperature [3], so that the equilibrium polarization M is limited to 0.31% per tesla. Until recently, only two methods have led to the achievement of (out of equilibrium) high nuclear polarization in a liquid, namely, fast condensation of an optically polarized gas [4] and fast melting of a solid polarized by a high field at low temperature [5].

Nuclear polarization in isotopic helium mixtures can reach high equilibrium values only for very small concentrations of helium-3, where the magnetic Fermi temperature of the system is very low, and the effect of M on some properties of such systems has been studied [6]. On the other hand, the susceptibility (per atom) of *saturated* solutions is comparable to that of pure helium-3 [7], so that “brute force” methods cannot produce high polarizations.

Fractional distillation is an efficient process used to reach a high degree of chemical purity starting from a mixture of species. It relies on the difference in the composition of two phases that are in equilibrium while they are circulated. The method of overpolarizing helium-3 by distillation described in this paper is based on two properties of the low-temperature phases of helium-3. The first is that the intrinsic nuclear-spin-relaxation times are sufficiently long that helium-3 is effectively a mixture of two separate species: $^3\text{He}\uparrow$ and $^3\text{He}\downarrow$. The second is that for two phases of helium-3 in equilibrium (for example, the pure liquid and its vapor in a magnetic field), the nuclear polarizations are in general different (crudely, they have different magnetic susceptibilities due to their very different densities). Together, these properties allow separation of different spin states by distillation [8]. In this work, the two phases are the concentrated and dilute phases of a helium-3–helium-4 mixture; the advantage over the liquid and vapor phases of pure helium-3 is that the density of the dilute phase remains fairly high down to $T=0$.

Principle of operation.—The operation of the apparatus used in the present experiment and described below is similar to that of a standard distillation column

[9], but it has a few specific features: First, the vapor, which usually travels up the column, is now replaced by a “gas” of helium-3 atoms traveling down the column in a background of superfluid helium-4 (the lighter rich phase floats on the dilute phase, so that the boiler is situated above the condenser). Second, due to the low viscosity and high density of the “gas,” the relative (osmotic) pressure drop and temperature change along the column are very small, and can be neglected in most situations. Finally, different spin states are not quite equivalent to different chemical species since nuclear-spin relaxation can flip the nuclear spin. A detailed model of the operation of a distillation column can be developed for this specific system [10], but we shall give here only simple arguments about the steady-state regime compatible with the experimental situation.

Schematically, the apparatus consists of two volumes, an upper boiler where atoms are “evaporated” (get dissolved) into the dilute phase and a lower condenser where droplets of rich phase are produced, and a tube (the distillation column) that connects the boiler to the condenser. A downwards flow of atoms in the dilute phase is thus balanced by a counterpropagating backflow of liquid. Since the temperature is nearly uniform over the system, the flow in each phase is constant along the column, and only magnetization is exchanged at the interface. If the flow is slow enough so that polarizations at each point of the column are close to equilibrium with each other (which in general means they have different polarizations), then a flow of atoms results in a flow of magnetization. In the following, we shall assume that the column itself works ideally, meaning that relaxation is negligible and that it is long enough to provide a large number of distillation steps. Finally, let us assume that the ratio X of the polarizations in the dilute and the rich phase is given by the ratio of the corresponding molar susceptibilities:

$$X = \chi_d / \chi_c. \quad (1)$$

Along the demixing line, X is larger than 1 for temperatures below 200 mK [7], so that a net flux of magnetization leaves the boiler and reaches the condenser. In a steady-state operation, these fluxes are balanced by the effect of relaxation in the boiler and the condenser. Assuming the relaxation process to be very efficient in the

boiler, the polarization will be at thermal equilibrium with a value m_{eq} in the dilute phase. At the boiler end of a long enough column, polarization gradients are small and the magnetization current is only due to the circulation of atoms. If m is the polarization, and T_c and T_1 are the circulation and nuclear-spin-relaxation time constants in the condenser, respectively, overall conservation of magnetization can be written

$$\frac{m_{\text{eq}}}{T_c} \left(1 - \frac{1}{X} \right) + \frac{m_{\text{eq}} - m}{T_1} = 0, \quad (2)$$

so that the enhancement factor is given by

$$\frac{m}{m_{\text{eq}}} = 1 + \frac{X-1}{X} \frac{T_1}{T_c}. \quad (3)$$

This result is actually an upper limit, and the effect of relaxation, diffusion, or incomplete magnetization exchange in the column can only decrease this value.

Apparatus.—The cell in which the distillation experiment has been performed is sketched in Fig. 1. It consists of two volumes inside an epoxy (Stycast 1266) container, connected by a coiled tube. The upper chamber B (the boiler of the still) is partly filled with a liquid-helium mixture. The proportion of helium-3 in the mixture is about 50%, so that below 0.5 K, the liquid is phase separated. Below 100 mK, where the best results are obtained, a nearly pure helium-3 phase floats in B on top of a 7% dilute solution. The heat input due to the electric heater H drives the dissolution of helium-3 atoms: Typi-

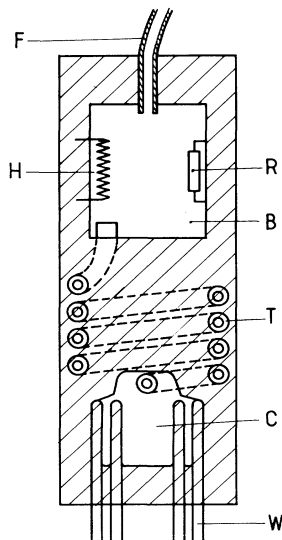


FIG. 1. Schematic of the experimental cell. It consists of two volumes in the interior of an epoxy block, and a connecting coiled Teflon tube (see text). F : fill line; H : electric heater; R : carbon-resistor thermometer, in boiler B ; C : condenser; T : distillation column. Copper wires W are connected to the dilution refrigerator. The outer diameter of the cell is 1.5 cm.

cally, powers of a few microwatts are used, corresponding to circulation rates of a few micromoles per second. The temperature is monitored using a 100- Ω Matsushita carbon resistor. The fill line F is carefully heat sunk to the various stages of the dilution refrigerator in order to minimize the uncontrolled heating in the boiler due to heat leaks along the line. In the bottom condenser C , droplets of nearly pure helium-3 are nucleated close to the cooling wires W that are connected to the refrigerator. This rich liquid would accumulate in the upper part of the condenser, but is quickly evacuated through the orifice of the connecting tube T that opens close to the top of C .

The enameled copper wires W are arranged using a coil foil technique: Over 200 wires provide a cooling area of 0.3 cm² in a volume of 0.5 cm³. This geometrical arrangement has been chosen in an attempt to allow a large circulation rate at low temperature and a long relaxation time in the condenser, so as to maximize the enhancement predicted by Eq. (3). The circulation rate is limited by poor thermal contact between the liquid mixture and the cooling wires; the Kapitza temperature jump at the interface accounts for the temperatures measured in the liquid: 77 and 93 mK for 1.2 and 3.0 μ W of heating in the boiler, the wires being kept at 40 mK. Relaxation can occur either on the walls or in the bulk of the liquid. Intrinsic bulk relaxation in pure helium-3 can be as short as a few minutes in the temperature range of this experiment [11]; for this reason the condenser was designed to trap very little of the rich phase, contrary to the boiler where short relaxation times are required. On the other hand, bulk relaxation time in the dilute phase is expected to be longer, but in order to minimize the wall relaxation rate, we kept the ratio of cooling area to liquid volume as small as possible in the condenser. Let us mention here that it would probably be useless to try to increase the cooling area using sintered metal powders: The heat has to be extracted from the mixture where condensation takes place, and no droplets of the rich phase can be nucleated and grown in a restricted geometry due to interfacial-tension effects. For the present cell, wall relaxation turned out to be the limiting factor in this experiment, and will be discussed later.

The distillation column itself is the tube T connecting the boiler to the condenser. It is made of a coiled Teflon tube (0.8 mm i.d.) that has been chemically etched on the outer surface before the epoxy was cast on to it. The tube has a slope of 10° instead of being vertical: This allows a longer column in a limited space and at the same time slows down the refluxing pure liquid. The exact nature of this backflow is not known: It may be a fairly regular "tube" of pure helium-3 filling the upper part of each section of the column, or possibly a chain of droplets traveling independently and not wetting the wall. A smaller column was also tried (0.32 mm i.d.), but interfacial tension between phases prevented any backflow of the rich phase below 600 mK.

Polarization measurements are made using pulsed NMR as described in Ref. [7]; a field gradient can be applied to map the polarization in the cell, allowing independent monitoring of its evolution in the boiler, the column, and the condenser.

Wall relaxation.—The inner surface of the condenser has been prepared following a procedure reputed to provide long wall relaxation times in high magnetic fields [12]: After machining, the rough inner surface is coated using a small amount of hot epoxy, and so are the cooling wires. In our experiments, it was impossible to get long wall relaxation times in epoxy containers: Typical values in the condenser of 1 min at $T=100$ mK in $B=1$ T were measured, and T_1 was found to be roughly proportional to T and B as could be expected for wall relaxation [13]. On the other hand, despite a worse geometry, T_1 in the Teflon distillation column was more than 20 times longer. The reason that relaxation times on epoxy are so short in our experiment is still not clear, but might be related to the difference of packaging for the catalyst of the epoxy (glass bottle in Europe, metal can in America).

Various attempts have been made, but no polarization enhancement was ever observed in the cell until we coated the surfaces of the condenser with molecular hydrogen. A low-temperature rf dissociator [14] was used to load the distillation cell with atomic hydrogen, which recombines preferentially in the condenser (the rest of the cell is kept warmer). After a few days of coating, the cell was filled with liquid-helium mixture and T_1 values of about 1 h at $T=100$ mK in $B=4.7$ T were obtained.

Results.—All the results presented here have been obtained with a hydrogen-coated condenser. The evolution of magnetization in the condenser is monitored using non-

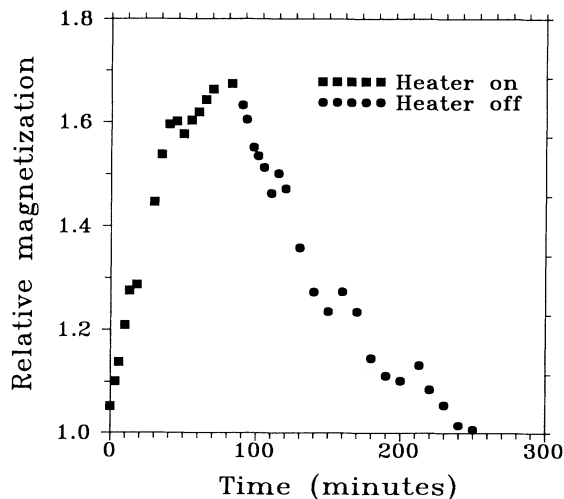


FIG. 2. Time evolution of the magnetization in the condenser, when the heating power is applied (squares) or turned off (circles). The temperature is 130 mK during the heating period, 100 mK otherwise.

destructive small-angle NMR pulses. Results shown in Fig. 2 have been obtained using $4 \mu\text{W}$ of heating power, corresponding to a circulation rate of $3.6 \mu\text{mole/s}$. As soon as the heating power is turned on in the boiler, the polarization increases. Once the power is turned off, the signal decays back to its equilibrium value with a time constant resulting from local relaxation and diffusion to the boiler.

The enhancement factors obtained for various heating powers and temperatures are plotted in Fig. 3 as a function of the combination of the heating power and the temperature of the liquid that is expected to be the relevant parameter from Eq. (3). The values for the ratio X of the susceptibilities have been measured independently [7], and the latent heat of dissolution is used to compute flow rates. A maximum enhancement factor of 3.5 was obtained, clear evidence of the efficiency of the distillation process. In addition, the results roughly lie on a straight line, its slope corresponding in Eq. (3) to a relaxation time of $4 \text{ s}/\mu\text{mole}$, i.e., about 4000 s in the condenser at 100 mK. This is in good agreement with the independently measured values for T_1 .

Additional measurements have been performed at lower magnetic fields where T_1 is shorter, and consistently smaller enhancements have been measured. No clear enhancement could be measured above 200 mK, but a weak reversed effect was observed at 450 mK: Polarization in the condenser decreased when distillation was performed, as is predicted by Eq. (3) for $X < 1$.

In conclusion, a clear polarization enhancement effect was demonstrated in this experiment, in good agreement

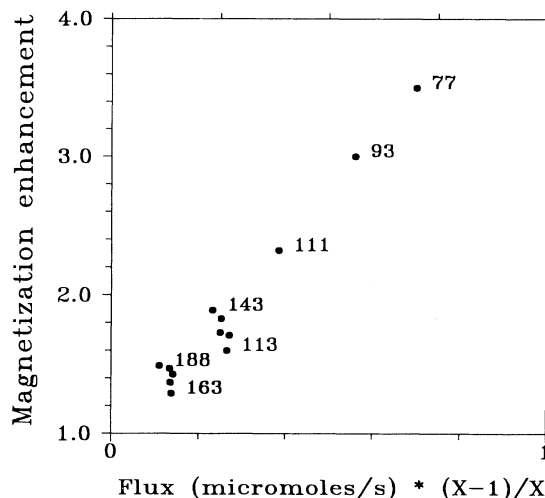


FIG. 3. Ratio of the stationary magnetizations recorded for fixed boiler heating to the corresponding equilibrium magnetizations, as a function of the relevant parameter of Eq. (3). X is the ratio of magnetic susceptibilities defined by Eq. (1). The numbers labeling the points refer to the temperature in millikelvin.

with the prediction of a simple model. Actual polarization was still low (about 5%), but we believe that the efficiency of the process could be improved, and that distillation might become an efficient method for preparing highly polarized liquid helium-3. Higher circulation rates, longer relaxation times, and a larger ratio of susceptibilities are required, and a possible way lies in performing an experiment at high pressure, and/or using different materials to overcome the relaxation problem.

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