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Boundary magnetism in liquid ^{3}He at very low temperatures

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Abstract. The low-temperature magnetic susceptibility of normal and superfluid ^{3}He confined between mylar foils spaced 4·0 μm apart shows a large and field-dependent enhancement over the bulk Fermi liquid magnitude. The excess susceptibility disappears when the liquid is doped with 0·5% ^{4}He. The reason for the excess is unknown. We also studied the proton resonance of the mylar substrate and obtained spin polarizations large enough to permit the direct observation of double spin-flip RF absorption.

We have observed that the nuclear magnetic susceptibility of liquid ^{3}He confined in a large stack of mylar plates increases to values much larger than that of bulk liquid when cooled to very low temperatures. An initial report of this effect was made by Ahonen *et al* (1975b) in a post deadline paper of LT 14. At the time the susceptibility increase was attributed to a possible condition of the superfluid B phase for liquid contained in very small channels. Our more recent measurements, reported in this work, show that the effect exists even in the normal liquid and that the effect is unambigously a boundary phenomenon. The physical cause of the effect remains a puzzle. We also made a brief investigation of the proton resonance of the plastic environment of the chamber.

The measurements were conducted in a nuclear demagnetization cryostat which could cool the liquid ^{3}He to 0·7 mK. The experimental arrangement is illustrated in figure 1. The NMR pick-up coil was wound around a cylindrical form containing a stack of 500 mylar plates, or foils, with an average spacing of 4·0 μm. Each plate was 3·6 μm thick. The entire assembly of mylar plates, the NMR coil and a graphite support structure was immersed within a cylindrical cavity of the nuclear cooling apparatus and the temperatures monitored with a platinum NMR thermometer. A general discussion of the techniques for measuring and maintaining low temperatures with this apparatus is to be published elsewhere (Ahonen *et al* 1976).

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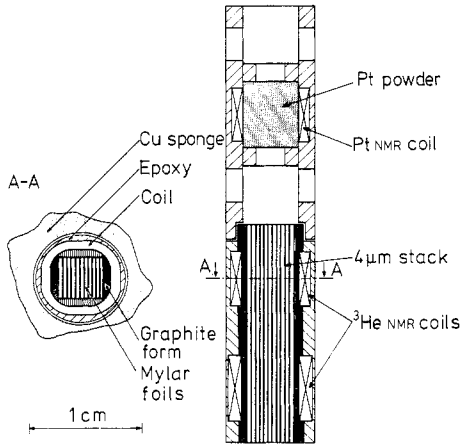

Figure 1. A schematic drawing of the experimental chamber.

During the course of the work the issue of how much surface ^{3}He could be 'seen' by the NMR coil became an important issue. Consequently, we performed nitrogen adsorption experiments using the BET method† to measure the surface area of a replica of the epoxy coil form containing the pitch-bonded graphite and mylar sheets. We found that the surface area within the coil is essentially only that of the obvious external surfaces, primarily the mylar sheets and mylar spacers. The pitch-bonded graphite is not a porous material. Separate BET measurements in a cell filled only with the graphite showed that the graphite has a negligible internal surface area. The complete sample cell for the ^{3}He has a volume of 8 cm^3 and, of course, the dominant surface area is that of the sintered copper sponge used for heat transfer from the nuclear demagnetization stage. The surface of the entire cell has also been determined to be 30 m^2 through nitrogen adsorption measurements of a matching copper sponge.

The ^{3}He susceptibilities were measured using both pulsed and CW NMR techniques with no significant difference in the results. The pulsed technique proved to be somewhat simpler to use in practice because of the rather irregular lineshapes associated with the geometry of the specimen of ^{3}He. The amplitude of the free-induction decay of the nuclear precession signal, $f(t)$, following a pulse applied near the resonance frequency, γH_0, in an applied field, H_0, is the Fourier transform of the dissipative part of the nuclear susceptibility $\chi''(\omega)$:

$$f(t) = A \int_{-\infty}^{\infty} \exp(-i\omega t)\, \chi''(\omega - \gamma H_0)\, d\omega$$

where A is a constant. The total, or DC, susceptibility is proportional to the integral $\int[\chi''(\omega)/\omega]\, d\omega$, so that the initial amplitude of the free-induction decay, $f(t = 0)$ also gives a measure of the total susceptibility.

The method we used is similar to that described by Ramm *et al* (1970) in their measurement of the liquid susceptibility. A gated integrator was used to read the amplitude of the free-induction signal in a narrow time interval after the termination of the

† The initials BET are for the method reported by Brunauer, Emmett and Teller (1938). More recent discussions of the method may be found, for instance, in several articles referred to by Daunt *et al* (1973).

tipping pulse. In our case we had the added inconvenience that the free-induction decay envelopes were temperature-dependent. They were approximately exponential in shape with the characteristic decay time, T_2, decreasing by approximately 50% in the temperature interval between 15 mK and 1 mK in the normal phase. In order to compensate for this effect the free-induction amplitude at each temperature was sampled at several different times so that the signal at $t = 0$ could be obtained through an exponential extrapolation. Typical integration gate widths were 60 μs long with the signal sampling beginning 60 μs and 120 μs after the termination of the tipping pulse. The minimum decay time was of order 400 μs so that the errors in the method should be quite small for the liquid in the normal phase. Without this compensation we would have underestimated the relative susceptibility change by about 15% at 1 mK using a sampling method with a single integration gate reading at the earliest convenient time. In the cases where small quantities of ^4He were added to the sample, the free-induction envelope shape was independent of temperature so that the relative susceptibility changes were determined using a single sampling pulse at each temperature.

The essential features of our results are illustrated in figure 2 where the low-temperature susceptibility is plotted. At temperatures between 15 mK and 50 mK we

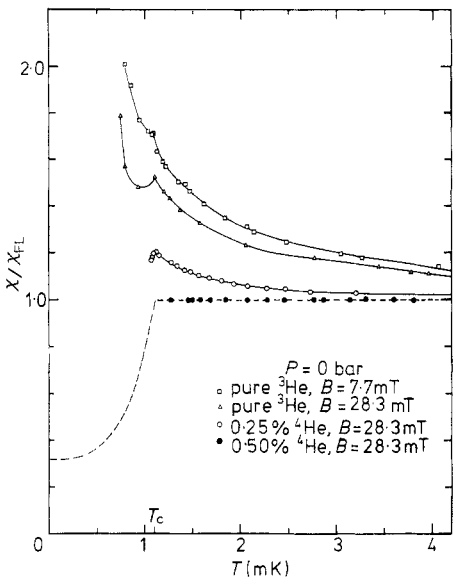

Figure 2. The susceptibility of liquid ^3He in the narrow channel apparatus. The data are from pulsed NMR measurements for the liquid at a pressure of 0 bar. The value of χ_{FL} was determined from measurements at temperatures greater than 15 mK.

observe no change in the liquid susceptibility. We take this magnitude to be the well known Pauli susceptibility of the bulk Fermi liquid. As the temperature is decreased toward 1 mK the susceptibility of pure liquid ^3He increases. The relative change for pure ^3He in two different magnetic fields and with various quantities of ^4He doped into the liquid measured in the larger magnetic field are shown in the figure. The transition to the

superfluid B phase takes place at 1·1 mK at the pressure of these measurements, 0 bar†. In the bulk liquid, the superfluid susceptibility is known to decrease to about $\frac{1}{3}$ of the normal Fermi liquid value for temperatures much less than T_c (Corruccini and Osheroff 1975, Ahonen *et al* 1975a). The relative size of the susceptibility enhancement we observe is decreased as the magnetic field increases.

The excess susceptibility has also been observed to exist in the liquid at higher pressures. It is easier to study the effect at 0 bar (or saturated vapour pressure) because the onset of the superfluid transition with the attendant B phase susceptibility drop tends to mask the effect. The areas of CW absorption signals were measured as a function of temperature at liquid pressure intervals of approximately 5 bar up to a pressure of 30 bar and the result remains qualitatively the same. The excess seems to scale very well with a model assuming that the absolute magnitude of the excess at a given temperature remains constant while the bulk liquid susceptibility varies with density in the way predicted by the experimental Fermi liquid corrections (Ramm *et al* 1970).

We repeated the experiments with the external field both perpendicular and parallel to the mylar foils and found that the effect was independent of the orientation of the static magnetic field.

Since our results for the pure liquid bore little resemblance to the usual bulk liquid properties, we followed the suggestion of Joe Serene of coating the walls with ^{4}He to try to reconstitute the usual behaviour. Because of the larger mass, ^{4}He has a larger van der Waals attraction to surfaces than ^{3}He and at these temperatures essentially complete phase separation is expected, so that the ^{4}He should be entirely located on the various surfaces of the chamber (Evenson *et al* 1968). The concentration 0·25% was based upon a crude estimate of the quantity of ^{4}He required to cover the various surfaces of the cell with a monolayer of ^{4}He. We do not know how uniformly the ^{4}He is deposited upon the assortment of surface materials within our cell. With the concentration 0·25% of ^{4}He, the cooling of the apparatus was impeded in no measurable way but the size of the excess susceptibility was substantially reduced, as shown in figure 2.

When the amount of ^{4}He in the sample was doubled to 0·5%, the low-temperature susceptibility increase completely disappeared. In this case we did not cool to the superfluid transition, primarily because of extra eddy current heating accidently introduced during the demagnetization process, rather than any large increase in the time constant for cooling.

The disappearance of the excess susceptibility in the ^{4}He doping experiments shows that the surface layer plays a dominant role in the low-temperature enhancement of the pure ^{3}He polarization.

Because of the way in which the ^{4}He affects the nuclear magnetization, it is tempting to interpret the initial doping as a quantity producing slightly less than a monolayer coverage on the mylar foils and the second doping a coverage of less than two layers. We do not know enough about how the ^{4}He is really deposited or have a sufficiently quantitative knowledge of our surface areas to claim that we know this to be the case.

The interpretation of the excess susceptibility is quite a puzzle. There have been a number of studies of the susceptibility of ^{3}He monolayers and films deposited on various materials. Probably the most systematic body of work is that by the group at Sussex University using vycor glass (Evenson *et al* 1968, Rolt and Brewer 1972). The surface layer of helium is deposited with a density much higher than that of the bulk liquid and

† We repeated the measurements of transition temperature versus liquid pressure using the platinum powder thermometer and inexplicably found that the transition temperatures were systematically higher than those previously reported (Ahonen *et al* 1974). A more complete account will be given elsewhere.

the susceptibility follows Curie's law rather than having the Fermi liquid behaviour of the bulk. The second layer in vycor glass behaves like a liquid of high density and the subsequent layers take on the bulk properties. We can easily estimate the expected contribution of the solid layer to the susceptibility we should measure at 1 mK with the liquid at 0 bar. Between two square slabs of area 1 cm^2 spaced 4·0 μm apart, there should be 2×10^{15} atoms of 'solid' and $6{\cdot}2 \times 10^{23} \times (4{\cdot}0 \times 10^{-4}/36{\cdot}84) \simeq 6{\cdot}7 \times 10^{18}$ atoms of liquid, where we have used typical surface densities (Daunt *et al* 1973) of 10^{15} atoms per cm^2 and the molar volume of bulk liquid at zero bar (Wheatley 1975†). Thus the fraction of atoms with a solid behaviour that we may expect to measure is $3{\cdot}0 \times 10^{-4}$. In the actual case of our measuring coil, the liquid outside the coil contributed approximately 50% of the signal but the surface area of the mylar is roughly double that of this model calculation because of the cracks between the mylar spacers at the end of ^3He slabs (see figure 1). The liquid at this density (Ramm *et al* 1970) has an effective spin (or Curie law) temperature of 359 mK. Thus the solid contribution at 1 mK would be expected to be 359 times that of the liquid per atom. We therefore expect an excess susceptibility from the solid layer to be about 11% at 1 mK. In the lowest magnetic field of our experiments we measured an effect one order of magnitude larger than this. The sintered copper sponge around the outside of the coil has a much larger surface area than the mylar, of course, but previous experiments (Ahonen *et al* 1975a) with open NMR coils of approximately the same geometry have not shown the susceptibility enhancement we observe here. The electrical conductivity of the copper sponge screens the RF away from the ^3He on the sintered surfaces. The effect is clearly related to the geometry of the material within the NMR coil but is too large to be understood in terms of a surface solid alone.

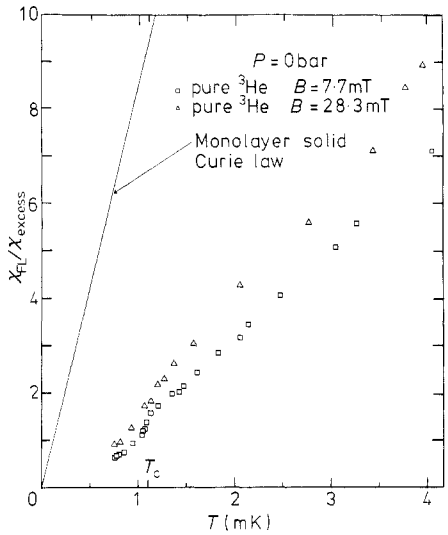

Figure 3. The inverse of the normalized excess susceptibility versus temperature. The data are obtained from the experiments with pure ^3He shown in figure 2.

Figure 3 shows another representation of the data. The inverse of the susceptibility excess, normalized by the high-temperature susceptibility, $|(\chi - \chi_{FL})/\chi_{FL}|^{-1}$ is plotted against the temperature. The figure shows the data for pure ^3He taken in the two mag-

† For various bulk properties of liquid ^3He, refer to tables 3–6 in this review article.

netic fields and is the same as that of figure 2 for liquid at 0 bar. Below the superfluid transition temperature at 1·1 mK, the bulk liquid susceptibility is assumed to decrease with respect to T/T_c in the manner previously measured (Ahonen *et al* 1975a) at 18·7 bar. The apparent deviations of the data from a straight line in these plots is most likely related to a deterioration below T_c of the exponential extrapolation of the magnetization time decay which we used in determining the susceptibility. The lineshape of the superfluid is extremely complex in this geometry. If the data shown in figure 3 had been obtained from a specimen of solid ^{3}He, the interpretation would probably be that the material is about to undergo a *ferromagnetic* phase transition near 0·5 mK. The high-temperature behaviour of a magnetic system with a ferromagnetic exchange interaction can be approximated with a Curie–Weiss law in the form $\chi = C/(T - \theta)$, where θ is a positive constant of the same order as the Curie temperature and C is the Curie constant. Such plots in solid ^{3}He have a *negative* temperature intercept at $\chi^{-1} = 0$, leading to the widespread assumption that the magnetic ordering of solid ^{3}He is antiferromagnetic (see, for instance, the review by Trickey *et al* 1972). In this case such interpretations are implausible because the size of the excess susceptibility is *much* too big. The slope of the Curie law for a monolayer of solid ^{3}He coating the surfaces within the coil is also plotted in figure 3. Roughly five times more surface area than we can account for in our cell is required to produce the measured high-temperature susceptibility excess if we are to attribute it to the behaviour or the solid-like surface alone.

Even prior to these experiments, Creswell and Brewer (1974) predicted that an excess susceptibility might be observed for liquid ^{3}He in this geometry. They suggested that the atoms in the second layer from the surface, having a factor of 3 greater polarization than the bulk because of their higher density, and hence a lower Fermi temperature, would tend to travel a mean free path from the surface before scattering mechanisms would cause them to take on the bulk liquid polarization. The susceptibility characteristic of the higher-density surface liquid might thus be expected to decay exponentially over the means free path length from the surface. For liquid at 0 bar, the mean free path, using the data for thermal diffusivity in Wheatley's (1975) tables, is $\lambda \sim 30\ \mu\text{m} \times (1\ \text{mK}\ \text{T}^{-1})^2$. This is a much greater length than the separation, x, between our mylar foils, 4 μm. In the limit $x \ll \lambda$, all of the liquid would be expected to take on the polarization of the higher-density liquid, up to a factor of 3 larger than the bulk polarization. At higher temperatures, the excess susceptibility would be expected to decrease exponentially as $\exp(-x/\lambda) \simeq \exp|-0{\cdot}1(\text{T mK}^{-1})^2|$. Since roughly 50% of the bulk NMR signal comes from liquid not inside the coil, and hence not affected by the stack geometry, the predicted magnitude of the effect suggested by Creswell and Brewer at 1 mK for liquid at 0 bar is roughly the same as we measure. However, the model fails to predict most of the other aspects of the experiment. No field dependence is expected in the model and the relative size of the effect clearly decreases as the field is increased. The inverse of the measured excess susceptibility increases linearly with temperature, whereas the model predicts that it would increase as $\exp(aT^2)$ (where a is a constant of order 0·1). At higher pressures, the model predicts that the effect should almost disappear because the mean free path decreases by a factor of 5 and the difference between the second layer density and bulk density decreases, whereas the excess susceptibility can still be seen easily at a pressure of 30 bar.

Creswell and Brewer considered the possibility that the atoms of the solid surface layer might produce similar polarization in the bulk, but rejected the idea because the surface atoms are expected to be tightly bound to the substrate by a strong van der Waals attraction. However, most of the objections to the mean free path argument

disappear if the surface atoms have even a small probability of appearing as part of the bulk polarization. Not only do the surface atoms have a magnetization 300 times that of the bulk atoms, they also suffer dipole interactions with the material in the mylar substrate such as electronic impurities and even the protons of the plastic. It is conceivable that the strength of such interactions might depend upon the extent of the substrate polarization and hence upon the strength of the applied magnetic field. Electronic impurities, for instance, might tend to have a more saturated magnetization in the experiment in the larger magnetic field illustrated in figure 1 and thus not be as likely to pump the spin polarization of ^{3}He atoms travelling back into the liquid. It is difficult to make a serious speculation without a great deal more knowledge of the surface interactions.

There are several other aspects of these experiments which we would like to report here because of the possible usefulness in the interpretation of these data and possible use in other magnetic studies at very low temperatures. With regard to the condition of the mylar substrate, we made a brief study of the CW proton resonance at the frequency 930 kHz. Interpretation of these measurements is complicated by the fact that protons were contained in both the epoxy of the coil form and in the mylar sheets. At the lowest temperatures, the proton signals were enormous. The total proton absorption signal was three orders of magnitude larger than the ^{3}He signal and had a width at half maximum of about 1·5 mT.

An unusual feature of the proton experiment is that we were able to make a direct observation of the satellite line occurring at the field $H_0 = \omega/2\gamma_p$, where γ_p is the proton gyro-magnetic ratio. The satellite corresponds to an absorption in which one RF photon flips two spins. The double spin-flip interaction is well known in NMR literature (Anderson 1962) but cannot be observed directly under ordinary circumstances because the probability for such transitions is of the order $(H_d/H_0)^2$ less than that for the single-spin interaction of the main resonance line. H_d is the strength of the nuclear magnetic dipole field ($\sim\gamma_p\hbar/a^3$ where a is the distance between nuclei). In our case the polarization was sufficiently large that the satellite line was almost the size of the signal of the ^{3}He under investigation.

Using the initial polarization of the protons before the demagnetization, where they had been held at a constant temperature for many hours to define a spin temperature of roughly 17 mK, we observed the changes in the proton temperature in a demagnetization cycle similar to those used in the studies of the ^{3}He. Immediately after the demagnetization, the proton temperature lagged behind that of the platinum powder immersed in the liquid ^{3}He. Several hours after the changes in the demagnetization field had stopped, the protons had a spin temperature of 2 mK while the platinum was less than 1 mK. Then, following heat pulses into the liquid, the proton signal was observed to decrease rapidly at first and then gradually drift toward colder temperatures (an increase in signal strength). The time constant of the slow drift was of the order of hours, while that of the initial response seemed to be comparable with the platinum thermometer. The simplest interpretation of these measurements is that the protons in the mylar actually followed the temperature changes of the ^{3}He rather rapidly in times of the order of seconds while the protons deep within the epoxy were probably still cooling as long as the ^{3}He temperature was less than the initial 17 mK. The experiments suggest that thin sheets of mylar, and probably other plastics, have reasonably strong thermal contact with liquid ^{3}He and short spin–lattice relaxation times. We did not repeat the proton experiments with the ^{4}He-doped specimens of ^{3}He in the sample chamber.

We made no systematic study of changes in thermal time constant with the ^{4}He

doping but we were rather surprised that the liquid cooled as easily as it did. In the case of 0·5% doping of ^{4}He, the time constant for equilibrium between the nuclear demagnetization stage and the liquid helium was less than a factor of 2 longer than that observed with pure ^{3}He. It is generally believed that the primary mechanism for heat transfer into liquid ^{3}He at the lowest temperatures is a magnetic surface interaction (Avenel *et al* 1973). The Kapitza resistance associated with phonon heat transfer would be expected to produce thermal time constants an order of magnitude longer than any of those we observe in these experiments (see, for instance, Lounasmaa (1974) ch 9). The magnetic interaction presumed to be responsible for the heat transfer varies as r^{-3}. If a monolayer of ^{4}He increases the effective range of the magnetic interaction by a factor of at least two, which seems plausible, the resistance to heat transfer might be expected to increase by an order of magnitude†. No such increase was observed.

In summary, we have reported what we feel to be a rather interesting phenomenon in liquid ^{3}He bounded in a narrow slab geometry. The central results are that there is a field-dependent enhancement of the pure ^{3}He magnetic susceptibility over the bulk Fermi liquid value. The excess susceptibility obeys something like a Curie–Weiss law with a positive temperature intercept of 0·5 mK. The enhancement disappears when ^{4}He is doped into the liquid ^{3}He. The experimental environment was accidental, rather than one really designed for these studies. Progress in understanding these effects will probably require measurements in much better defined geometries with well characterized substrates.

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† In the case of the thermal contact between CMN and liquid helium, Black *et al* (1971) found that a ^{4}He monolayer made a great increase in the boundary resistance.