Nuclear Alignment in Liquid and Solid $^3$He ($^\dagger$).

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$^3$He and $^4$He represent the only substances that remain liquid at the absolute zero. It is of considerable interest, therefore, to observe the way in which each becomes ordered as the absolute zero is approached. In the case of $^4$He as is well known, the condensation into a superfluid state, which begins to take place at the lambda point, is thought to be, as was first suggested by London, an ordering in momentum space analogous to the condensation which would take place at low temperature in an ideal Bose-Einstein gas. Since $^3$He, on the other hand, would be expected to obey the Fermi-Dirac statistics, it is of particular interest to observe the extent to which its behavior as the absolute zero is approached is analogous to that of an ideal Fermi-Dirac gas.

In the talk which follows Dr. Weinstock will discuss the information which has been obtained on this subject from specific heat measurements. It is the purpose of this talk to discuss some nuclear magnetic resonance experiments designed to measure directly the behavior of the nuclear spin system of $^3$He as the absolute zero is approached.

At the absolute zero the nuclear spins of the $^3$He atoms must be ordered. In the absence of statistical or quantum mechanical exchange effects the nuclei would be expected [1] to become aligned at a temperature of approximately $10^{-7}$ °K due to the magnetic dipole-dipole interaction between nuclei. However, the spins of the particles of an ideal Fermi-Dirac gas of the same spin, density, and atomic mass as liquid $^3$He would begin to become anti-parallel

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aligned at temperatures of the order of 5 °K, the Fermi temperature for such a system, as the particles condense into the lowest energy levels. Since the particles thus aligned could not contribute to the magnetic susceptibility, this model would predict a nuclear magnetic susceptibility which deviates from the classical 1/T Curie law below 5 °K becoming finally temperature independent as the absolute zero is approached.

Since nuclear magnetic moments are extremely small, conventional methods of susceptibility measurements are difficult [2], although HAMMEL et al. [3] have demonstrated the absence of ferromagnetism in liquid 3He down to 1.2 °K by this method. Nuclear resonance techniques [4-6], however, offer a convenient means of measuring very small susceptibilities. If the sample under investigation is immersed in a steady magnetic field $H_0$ and is excited at the Larmor frequency $\nu_0(H_0)$ of the nuclear spins by a weak radio frequency field at right angles to $H_0$, then transitions will be induced among the energy levels of the spin system. For the $^3$He nucleus there are two allowed orientations with respect to the field, separated in energy by $2\mu H_0$, where $\mu$ is the magnetic moment of the $^3$He nucleus. Once thermal equilibrium is attained, there will be a surplus of spins in the lower state, and, during resonance, power will be absorbed by the sample from the radio frequency field. The power absorbed is directly proportional to the difference in population of the two spin states and therefore to the static nuclear susceptibility.

We have succeeded [7,8] in measuring the temperature dependence of the nuclear susceptibility of $^3$He by observing the strength of the nuclear resonance absorption signal. Under the conditions of the experiment, the amplitude of the nuclear resonance signal, corrected for its small effect on the $Q$ of the coil, is proportional to the nuclear volume susceptibility [4,5,7]. The experimental results for $^3$He under its saturated vapor pressure are shown in Fig. 1. The molar susceptibility, $\chi$, has been calculated from the volume susceptibility using the density measurements of KERR [9]. The signal in the gas at 4.2 °K, where the susceptibility would be expected to be nearly classical, was used to normalize the data to the Curie curve. $\chi T$ has been plotted vs $T$ so that the Curie curve, 1, becomes a straight line parallel to the temperature axis. It is seen that the data fall between curve 1, and curve 3, the curve for an ideal Fermi-Dirac gas with a degeneracy temperature of 5 °K, appropriate for an ideal gas of the same density and atomic mass as $^3$He. For comparison, curve 2 is the curve for a Fermi-Dirac gas with a degeneracy temperature of 0.45 °K, arbitrarily selected to give the best fit to the data. The normalization techniques mentioned above using the gas at 4.2 °K are not sufficiently accurate to ascertain whether or not there is in reality a 5% departure from the Curie curve at 1.2 °K as would be expected from Curie curve 2. We have drawn in the dashed curve as the data would appear if normalized to the Curie curve at 1.2 °K. As will be discussed later, a com-
parison of susceptibility measurements as a function of pressure with the recent density data [10] gives some evidence that the degeneracy at 1.2 °K is less than 5%. The normalization indicated by the dashed curve will be used for comparing the data in Fig. 1 with the data taken under pressure.

![Plot of $\chi T/C$ vs. $T$. ($\chi$ = molar nuclear magnetic susceptibility of $^3$He, $T$ = absolute temperature, $C$ = normalizing Curie constant). Curve 1 represents the Curie law expected from Boltzmann statistics, curve 3 represents an ideal Fermi-Dirac gas with the same density and atomic mass as liquid $^3$He ($T_0 = 5^\circ$), curve 2 represents an ideal Fermi-Dirac gas with a degeneracy temperature $T_0 = 0.45^\circ$K. The circles represent the experimental points. The dashed curve represents the experimental data normalized to the Curie curve at 1.2°.](image)

It appears from this experiment that the nuclear spins of liquid $^3$He line up antiparallel as would be expected of an ideal gas, but at temperatures an order of magnitude lower. At the lowest temperatures the susceptibility has become independent of temperature as expected of an ideal gas, but with a constant value about 10 times greater than the analogous gas model.

As will be pointed out by Dr. Weinstock in the following talk, the specific heat data also seem to indicate spin ordering below 0.5 °K, but does not bear the same type of relationship to an ideal gas shown by the susceptibility [11-13]. This difference has been stressed by Buckingham, who has pointed out that this implies the existence of strong spin dependent exchange forces tending toward parallel alignment of the spins which effect strongly the susceptibility, but not the specific heat. He has suggested [14] that, under certain conditions, one might even expect the exchange forces tending toward parallel alignment to exceed the statistical forces tending toward antiparallel...
alignment, resulting in a susceptibility greater than the Curie value. Brueckner [15] has presented a theory based on first principles which gives quantitatively these two types of alignment tendencies and predicts a low temperature value of the susceptibility in agreement with the experimental results. Several other theories [16-25] have been proposed to explain the susceptibility and specific heat data. Since Dr. Buckingham will discuss the theoretical aspects of this problem in a paper later this morning I will not discuss various theories further.

In 1951, before any of the experiments on the nuclear susceptibility had been performed, Pomerančuk [1] suggested that spin ordering would be expected to occur in liquid $^3$He at temperatures above 1 °K, but that spin ordering in the solid might not occur until $10^{-7}$ °K, the temperature for spin ordering due to spin-spin interactions between neighboring nuclei. If this were indeed the case, the entropy in the solid would be greater than the entropy in the liquid and one would have to heat liquid $^3$He to freeze it at constant temperature. Pomerančuk further pointed out that if this suggestion were correct and one compressed liquid $^3$He to solid $^3$He reversibly and adiabatically, the solid would cool to the order of $10^{-7}$ °K, or whatever temperature the spin in the solid become ordered.

In order to check this intriguing suggestion of Pomerančuk and to observe the behavior of the susceptibility in the liquid under pressure as well as in the solid, we have extended [26, 27] the susceptibility measurements to higher pressures including the solid. The pressure is applied through a long stainless steel capillary 0.01 cm I.D. Fig. 2 shows the susceptibility data at higher pressures including one curve in the solid. The unlabelled curve is the susceptibility for the liquid under its saturated vapor pressure. The data have been normalized to the Curie curve at 1.2 °K since measurements at this temperature when compared with the Los Alamos density data [10] indicate that the molar susceptibility remains constant as a function of pressure at this temperature. The possible small deviation from the Curie curve indicated from the gas calibration at 4.2 °K and shown in the first curve in this paper has been neglected.
The data in Fig. 2 show that the temperature at which the susceptibility falls below the Curie curve decreases with increasing pressure. This is in the opposite direction from that which would be expected for an ideal gas model. The curve for the solid agrees qualitatively with the prediction of Primakoff [28] that anti-parallel alignment would be expected in the solid at about 0.5 °K but disagrees with the suggestion of Pomerančuk [1] that spin alignment might not take place in the solid above 10⁻⁷ °K.

However, the curve shown is not the only curve we have obtained for the solid. In the earliest measurements, positive deviations from the Curie law were consistently observed, the solid indicating a tendency toward ferromagnetic behavior. At the lowest measured temperatures, the susceptibility was about 40% larger than the Curie value, rising rapidly with decreasing temperature.

At the present it is difficult to explain the peculiar behavior of the solid. The large change, by a factor of nearly 2, at the lowest temperatures in the susceptibility of the solid between our earliest and latest runs should be outside the experimental error in susceptibility and temperature measurements, especially since the measurements made on the liquid during each of these runs were always reproducible.

We believe that the explanation lies, rather, in some unknown change in the process of solidification, the magnetic properties of solid ³He being markedly dependent on some factor such as interatomic spacing, crystal structure, strains, etc., which can even cause the sign of the deviation from the Curie law to change. We have redesigned the apparatus so that solidification, which in the present apparatus with the long fine capillary took place during demagnetization, can be caused to take place under a wide variety of controllable conditions of temperature and pressure.

Despite the radically different behaviors observed for solid ³He in the earlier and later experiments, one very important fact does emerge. In each case deviations from the Curie law, indicative of spin alignment, occur at the same order of magnitude of temperature as in the liquid at melting pressure, indicating that interactions much stronger than the classical dipole interaction must occur in solid ³He.

It will be noted from Fig. 2 that the spin ordering in the solid occurs at slightly lower temperature than in the liquid. Hence, at any given temperature below about 0.4 °K it would appear that the spin entropy is somewhat greater in the solid than in the liquid. An attempt was made to determine whether or not the total entropy of the solid was greater than the total entropy of the liquid by allowing the solid to expand adiabatically into a liquid. It was found that heating occurred at the melting point for temperatures below about 0.4 °K, and cooling occurred above this temperature. This would seem to indicate that the entropy in the solid is greater than the entropy in the
liquid below 0.4 °K and that a minimum in the melting pressure curve should occur at this point, providing friction is not responsible for the heating.

When the experiment is performed on the solid which shows the anti-parallel alignment indicated in Fig. 2, the quantities of heat liberated below 0.4 °K are measured to be approximately equal to the temperature times a reasonable estimate of the entropy differences between the solid and liquid as determined from the susceptibility data. This would be expected in the case of a reversible expansion. On the other hand, when the adiabatic expansion experiments were performed during the earlier runs in which the solid exhibited a tendency toward parallel alignment, it was found that approximately four times as much heat was released as would be expected. This is another important difference between the two results obtained in the solid.

The large amount of heat liberated when the solid melted suggests an irreversible process in which some of the energy of compression was lost to heat. This suggests the presence of more strains or greater compression in the solid during the runs which showed a ferromagnetic tendency, and the possibility that the spin ordering in solid ³He depends critically on the degree of compression or on the presence of strains. If friction were responsible for the heating, then there had to occur a large change in the amount of friction between the runs showing parallel alignment and the runs showing anti-parallel alignment.

Grilly and Mills [29] have reported a phase transition in solid ³He. This solid-solid transition intersects the melting curve at 3.15 °K and occurs at decreasing pressures as the temperature is reduced. It is interesting to speculate on whether the peculiar behavior of the spin system in the solid below 0.2 °K is related to this phase change. In the experiment on melting mentioned above the expansion takes place suddenly when a pressure equal to the minimum in the melting pressure is reached and the capillary becomes unplugged. Onsager has pointed out that if the expansion in the parallel alignment case is from a high pressure phase of the solid directly to the liquid without forming the intermediate lower pressure phase, the expansion would be irreversible.

Fig. 3 is a graph of the spin lattice relaxation time, $T_1$, as
the liquid-solid boundary is crossed. The very great drop in the value of $T_1$ from 60 s to less than 2 s enabled us to tell easily whether the sample was liquid or solid. If part of the sample were liquid and part solid it should have been possible to saturate the liquid part of the line. Such a mixture was not observed. By observing continually the spin-lattice relaxation time as the pressure was released from the solid $^3$He, we were able to obtain a rough determination of the melting pressure curve. Our measurements are in agreement with those of Abraham, Osborne and Weinstock [30], showing a constant value of about 29 atm for the melting pressure below 0.4 °K. This does not preclude the slope of the curve becoming negative below 0.4 °K, since in our method just as in Abraham, Osborne and Weinstock's, the pressure of the minimum in the melting pressure curve would be observed for all lower temperatures.

The very short spin lattice relaxation time for the solid indicates that diffusion is still very great in the solid state. If we apply the theory of Bloembergen, Pound and Purcell [5], we find that the relaxation time is close to its minimum value and that the coefficient of self-diffusion falls between the limits

$$10^{-8} < D < 10^{-6} \text{ (cm}^2 \text{ s}^{-1})$$

We have constructed spin-echo apparatus for determining both $T_1$ and $T_2$ accurately in the solid as a function of $T$ and $P$.

In the process of investigating the susceptibility of $^3$He-$^4$He solutions, we have observed [31] a phase separation in which the $^3$He-$^4$He solution separates into two separate phases, one rich in $^3$He and the other rich in $^4$He. The $^3$He rich portion, being the lighter, floats to the top. This phase separation had previously been predicted independently by Sommers [32], Prigogine [33], and Chester [34]. Since the strength of the nuclear resonance signal is proportional to the number of $^3$He nuclei in the vicinity of the resonance coil, it is possible to use the nuclear resonance techniques to observe the phase separation and measure the number of $^3$He atoms in each phase. The sample container shown in Fig. 4 was designed for this purpose. It is divided

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Fig. 4. – Sample container for liquid $^3$He in nuclear resonance experiments designed to observe phase separation in liquid $^3$He-$^4$He solutions.
into three vertically arranged sections by a piece of bakelite (close hatch) around which the resonance coil is wrapped in three sections. Each section is joined by a hole. When this container is placed in a magnetic field having a gradient from top to bottom, and the magnetic field slowly modulated, resonance is observed at a slightly different time in each of the three cavities. Changes in the relative amplitudes of these peaks as a function of temperature give a measure of the concentration of $^3$He in each section of the sample container, hence a measure of the $^3$He concentration in each phase. Using this method on 40%, 50%, and 60% solutions of $^3$He in $^4$He we have arrived at the phase diagram shown in Fig. 5. The open circles represent the lambda point measurements of Daunt and Heer [35]. An interesting point, still to be determined, is whether these points represent the phase boundary or whether there is a lambda point in the upper phase.

K. W. Taconis and H. A. Fairbank will present further evidence on the phase diagram in papers later this morning. T. R. Roberts and S. G. Sydoriak [36] have also confirmed the existence of the phase diagram by vapor pressure measurements on $^3$He-$^4$He solutions. Professor Mendelsohn has reported that Professor Petskov and Miss Zinov'eva have made visual observations of the phase separation in $^3$He-$^4$He liquid mixtures below 1 °K, using a $^3$He cryostat.

In conclusion we would like to state that William B. Ard was largely responsible for the susceptibility measurements on liquid $^3$He under its saturated vapor pressure, the work forming the subject of his doctors thesis.

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REFERENCES