Interpretation of Recent Results on He^3 below 3 mK: A New Liquid Phase?

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(Received 5 September 1972)

It is demonstrated that recent NMR results in ^{3}He indicate that at 2.65 mK, the liquid makes a second-order transition to a phase in which the "spin-orbit" symmetry is spontaneously broken. The hypothesis that this phase is a BCS-type phase in which pairs form with l odd, $S=1$, $S_z=\pm1$ leads to reasonable agreement with both NMR and thermodynamic data, but involves some difficulties as to stability.

Recently Osheroff *et al.*[1,2] have reported some very intriguing thermodynamic and NMR measurements on mixtures of liquid and solid ^{3}He below 3 mK. They originally measured the rate of change of the pressure as a function of time, dP/dt, and observed that this quantity underwent a discontinuous fall by a factor of about 1.8 at a point A, corresponding to a temperature T_A of approximately 2.65 mK, and had a more complicated singularity at a point B, which probably corresponded to a temperature below 2 mK. This has been interpreted[1,3] as evidence for one or more phase transitions in the solid. However, subsequent NMR measurements[2] have produced a further surprise: At point A the signal attributed to the liquid portion of the sample starts to move away from the "solid" signal to higher values, while the liquid susceptibility stays at or close to the "Fermi-liquid" value. This shift continues up to point B, where in the absence of supercooling the signal suddenly jumps back to its original position and the susceptibility drops discontinuously by a factor of order 2. The difference of the squares of the "solid" and "liquid" signal frequencies was found to be independent of the external field and to be a function only of pressure (i.e., of temperature, since the experiments are done along the melting curve). Assuming that the slope of the melting curve is reasonably constant just below A, we have for T near T_A

$$(\nu_L^2-\nu_S^2)_{\mathrm{expt}}=B(1-T/T_A). \tag{1}$$

Assuming that (dP/dT) has no discontinuity at A (see below) we estimate[4] that B is approximately equal to 5×10^{10} Hz^2.

In this Letter we propose that the liquid has a second-order phase transition at A, and another transition, probably first order, at B, and investigate the nature of the ordered phase occurring between A and B (hereafter called phase II). We do not discuss, except very briefly, the nature of the transition at B or the phase below B, nor do we comment on the behavior of the solid, merely assuming that it has no special singularities between A and B.

We first demonstrate that phase II must be an ordered phase in which the direction of spin of any pair of particles is strongly correlated with their relative orbital motion; or in other words, the "spin-orbit" symmetry of the Hamiltonian must be spontaneously broken. To explain this, we write the total Hamiltonian of the liquid in the presence of the external magnetic field $\vec{\mathcal{H}}$ in the form

$$\hat{H}=\hat{H}_0+\hat{H}_z+\hat{H}_d, \tag{2}$$

where $\hat{H}_0$ includes the kinetic and ordinary (spin-independent) potential energy, $\hat{H}_z$ is the Zeeman term involving the external field, and $\hat{H}_d$ the nuclear dipole-dipole interaction. We note that both $\hat{H}_0$ and $\hat{H}_z$ are invariant with respect to rotation of the orbital coordinates relative to the spin coordinates: We can say this part of $\hat{H}$ possesses "spin-orbit symmetry."

Now the experimentally observed absorption is proportional to the susceptibility $\chi''(\omega)$, which obeys the two sum rules

$$(2/\pi)\int_0^\infty[\chi''(\omega)/\omega]d\omega=\chi, \tag{3}$$

$$(2/\pi)\int_0^\infty\omega\chi''(\omega)\,d\omega=-\hbar^{-2}\langle[\hat{M}_x,[\hat{M}_x,\hat{H}]]\rangle, \tag{4}$$

where χ is the static susceptibility and M_x the x component of the total magnetization (we assume the static external field is in the z direction and the rf field in the x direction).

If we now assume, in accordance with the experimental results, that in a uniform field $\mathcal{H}_0$ the liquid absorption has a very narrow peak at some value ω_L, we find from (3) and (4)

$$\omega_L^2=\gamma^2\mathcal{H}_0^2-\hbar^{-2}\langle[\hat{M}_x,[\hat{M}_x,\hat{H}_d]]\rangle/\chi \tag{5}$$

(γ is the gyromagnetic ratio of the free ^{3}He nucleus). Evaluating the commutator and assuming that the solid line stays at $\omega_S = \gamma\mathcal{H}_0$, we find (considering a unit volume of the system)

$$\nu_L{}^2 - \nu_S{}^2 = Q/4\pi^2\chi, \tag{6}$$

where

$$Q \equiv -3\gamma^4\hbar^2\langle \sum_{i\neq j} |r_{ij}|^{-5}(\vec{\sigma}_i \times \vec{r}_{ij})_x(\vec{\sigma}_j \times \vec{r}_{ij})_x + (\sigma_{ix}x_{ij} - \vec{\sigma}_i\cdot\vec{r}_{ij})(\vec{\sigma}_j\cdot\vec{r}_{ij})\rangle. \tag{7}$$

We notice that in an isotropic state of the system Q is just $-2\gamma^2\langle\hat{H}_d\rangle$.

Now, a finite value of Q implies that the state of the system is *not* invariant with respect to rotation of the orbital coordinates relative to the spins, despite the fact that $\hat{H}_0$ is. Moreover, the dipole forces themselves (which are the only forces in the problem not having this invariance) are far too weak to produce a value of Q of the observed order of magnitude. We are forced to conclude, therefore, that the "spin-orbit" symmetry of $\hat{H}_0$ is *spontaneously* broken in phase II. Crudely speaking, $\hat{H}_0$ makes it advantageous for all pairs of particles with the same total spin $\vec{S}$ to have also the same magnitude and direction of relative orbital angular momentum $\vec{L}$, but does not fix the direction of $\vec{L}$ relative to $\vec{S}$; the function of the very weak interaction $\langle\hat{H}_d\rangle$ is then to fix $\vec{L}$ relative to $\vec{S}$. We note that $\langle\hat{H}_d\rangle$ will always take a negative value, so it is natural that Q should be positive. The fraction of atoms able to participate in the ordering process is $\sim k_B T_c/\epsilon_F$; since both members of a pair must participate in order to contribute to Q, this gives $Q \sim (k_B T_c/\epsilon_F)^2 \times \gamma^4\hbar^2/a_0{}^6$ (T_c is the transition temperature, ϵ_F the Fermi energy, a_0 the interatomic spacing), which is of the right order of magnitude to produce the observed effect.

We now enquire as to the possible nature of the anomalous state. Although, obviously, one cannot exclude exotic states such as a standing spin-density wave, it is worth while to investigate the most obvious possibility, namely the long-predicted "anisotropic" BCS-type phase, with pairing in a state of nonzero relative orbital angular momentum l. We shall see that this gives at least qualitative agreement with the experimental data provided we assume that pairs form in a spin triplet state (odd l) but with $S_z = \pm 1$ only,[5] not with $S_z = 0$ also.[6]

It is straightforward, if tedious, to calculate the quantity Q for any BCS-type state (details of the computation will be given elsewhere). We consider here only temperatures near T_c and assume that the gap function is a matrix (in spin space) of the form (cf. Ref. 6)

$$\Delta_{\alpha\beta}(T;\vec{n}) = \Delta(T) f_{\alpha\beta}(\vec{n}), \tag{8}$$

where the unit vector $\vec{n}$ denotes direction on the Fermi surface, and the matrix f is proportional to a unitary matrix[6] and normalized so that the average of $ff^\dagger$ over the Fermi surface is 1. Using Eq. (6), we then find

$$(\nu_L{}^2 - \nu_S{}^2)_{\text{theor}} = 13.0\gamma^2(1 + \tfrac{1}{4}Z_0)(k_B T_c)^2(dn/d\epsilon)\ln^2(1.14\epsilon_0/k_B T_c)Fa(1 - T/T_c), \tag{9}$$

where Z_0 is the usual Landau parameter, $dn/d\epsilon$ the density of states of both spins at the Fermi surface in the normal phase, ϵ_0 an effective cutoff for the pairing interaction, a^{-1} is the average of $(ff^\dagger)^2$, and the dimensionless number F is given by

$$F \equiv \sum_{lm} \frac{d\Omega}{4\pi}\int\frac{d\Omega'}{4\pi} R^2(k)\Lambda_{lm}(\vec{k})K_{lm}(\vec{n},\vec{n}') \quad [\vec{k} \equiv k_F(\vec{n} - \vec{n}')], \tag{10}$$

$$K_{lm}(\vec{n},\vec{n}') \equiv \sum_{\alpha\beta\gamma\delta} \sigma_{\alpha\beta}{}^l \sigma_{\gamma\delta}{}^m f_{\alpha\gamma}(\vec{n}) f_{\beta\delta}{}^*(\vec{n}'), \tag{11}$$

$$\Lambda_{xx} = 0, \quad \Lambda_{yy} = -\Lambda_{zz} = (k_z{}^2 - k_y{}^2)/k^2, \quad \Lambda_{xy} = -\tfrac{1}{2}k_x k_y/k^2, \quad \Lambda_{xz} = -\tfrac{1}{2}k_x k_z/k^2, \quad \Lambda_{yz} = -2k_y k_z, \quad \Lambda_{ij} \equiv \Lambda_{ji}, \tag{12}$$

and the function $R(k)$ is a renormalization factor arising from the conversion of real particles into Landau quasiparticles. For a weakly interacting gas $R(k) \to 1$; for ^{3}He we know only that it tends to 1 as $k \to 0$ and is in general ≤ 1. We take ϵ_0/k_B to be[7] equal to 0.7°K and substitute values of the ^{3}He parameters measured[8] at 27 atm, and $T_c = 2.65$ mK. This gives

$$(\nu_L{}^2 - \nu_S{}^2)_{\text{theor}} \simeq 1.4 \times 10^{12} aF(1 - T/T_c)\ \text{Hz}^2, \tag{13}$$

which has the right temperature dependence and general order of magnitude. To evaluate the factors a and F we need first of all to determine the "shape" of the gap, that is, the functions $f_{\alpha\beta}(\vec{n})$. Since F vanishes identically for pairing in a spin singlet state, we must assume a spin triplet (hence odd l). Moreover, the experimental observation[2] that the spin susceptibility is practically the same as in the normal phase forces us to exclude any substantial pairing with $S_z=0$ (see below); we therefore have essentially a state of the Anderson-Morel (AM) type.[5] For a given assumed value of l, we proceed by first finding the family of degenerate solutions which minimizes the pairing energy (cf. Ref. 5), then invoking the dipole terms to break the degeneracy.[9] Finally, we substitute the value of f thus obtained in Eqs. (11) and (10) to find F. Unfortunately, this program can be carried out rigorously only if we know the renormalization factor $R(k)$, which we can only guess at. If we were to make the approximation, quite unrealistic for liquid ^{3}He, that $R(k)=1$ for all k, we should find that for $l=1$, $F=0.325$ and so (since for this l value $a=\frac{5}{6}$) the theoretical value of the NMR shift is about 6 times the experimental value. For real ^{3}He $R(k)$ is certainly less than 1 and, hence, we should expect F to be smaller, but it is difficult to estimate the effect quantitatively. Condensation in a higher-l state will also tend to depress F (and, to a lesser extent, a) and so improve the agreement with experiment. All in all, we can say that our hypothesis is at least not in obvious conflict with the NMR data.

The discontinuity in dP/dt at A can also be explained on our model. We follow the thermodynamic analysis of Horner and Nosanow,[3] but assume that there is little or no thermal transfer to the solid and that the *liquid* specific heat C has a discontinuity at A; then $(dP/dt)_{\text{above}}/(dP/dt)_{\text{below}} \leqslant C_{\text{below}}/C_{\text{above}}$, the equality holding if no heat is transferred to the solid. For a BCS-type transition the specific heat ratio is $1.55a+1$[5]; this is 2.29 for an AM-type P state and somewhat smaller for higher-l states. [This result is independent of the (unknown) form of $R(k)$.] Since the experimental dP/dt ratio is about 1.8, the agreement is reasonably satisfactory.

A major difficulty associated with the hypothesis presented here is that for a simple BCS model, in zero magnetic field, the AM state should always be unstable with respect to the Balian-Werthamer (BW) state[6] in which $S_z=0$ pairs are formed as well as those with $S_z=\pm 1$. (This is proved explicitly for $l=1$ in Ref. 6, and preliminary calculations make it at least extremely plausible for states of higher odd l.) Since the latter state has a quite strongly reduced susceptibility,[6,10] we have excluded it on experimental grounds, but it is not easy to see why it should become unstable[11] at fields as low as 31 G, when the "magnetic" energy lost through the reduced susceptibility is only a very small fraction of the total condensation energy. All we can suggest is that the pairing may be in a state of high l (say $l \geqslant 5$): In this case the *difference* between the condensation energies of the two states (which are proportional to their respective values of the quantity a) is likely to be a very small fraction of the condensation energy itself and could be outweighed by even a small magnetic term (or indeed conceivably even by the dipole energy itself).[12] Clearly, further theoretical work is needed to make this argument quantitative; more detailed experimental investigation of the behavior in very low fields might also help to clarify the situation.

If the hypothesis is correct, we should expect liquid ^{3}He in phase II to show all the phenomena (superfluidity etc.) predicted[5] for a BCS-type phase; we should also expect certain phenomena peculiar to a state of broken spin-orbit symmetry—such as resonance absorption of rf radiation polarized *parallel* to the external magnetic field when $\nu^2 \sim \nu_L{}^2 - \nu_S{}^2$.[13] A rather satisfying test of the details of the hypothesis, which would also help to identify the l value, would be a careful comparison of the experimental and theoretical values of $(\nu_L{}^2 - \nu_S{}^2)(T)$ as a function of T over the whole range A to B. However, neither the theoretical computation nor the experimental temperature measurement is a simple task.

As to the phase below B, we can conclude from the absence of an NMR shift that it does *not* have broken spin-orbit symmetry and hence is presumably not a triplet BCS phase. It could conceivably be a singlet BCS phase, but is equally likely to be something as yet unknown to theory.

I am very grateful to Bob Richardson for discussing his group's results before publication, and to Mike Moore and Mike Richards for numerour helpful discussions.

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[7] This estimate is obtained by multiplying the value found at vapor pressure by P. Morel and P. Nozières [Phys. Rev. 126, 1909 (1962)] by the ratio of the spin diffusion lifetime at 27 atm to that at vapor pressure [J. C. Wheatley, in *Quantum Fluids*, edited by D. F. Brewer (North-Holland, Amsterdam, 1966), p. 206]. Clearly, the result is fairly insensitive to error here.

[9] Note that the dipole energy is proportional to minus an expression identical to F, but with Λ_{ij} replaced by $\delta_{ij} - 3k_i k_j/k^2$.

[10] As well as an NMR shift comparable to the AM state.

[11] In fact, there is probably a continuous transition from one type of state to the other as the field increases, but our argument still goes through qualitatively.

[12] A further possibility is that particle-particle scattering may upset the stability of the BW state relative to the AM state.

[13] The ratio $\nu_\parallel^2/(\nu_L^2 - \nu_S^2)$, when $\nu_\parallel$ is the frequency at which rf radiation parallel to the external field is absorbed, should be an important indicator of the precise nature of the state (its l value etc.). For an isotropic state it is clearly 1; for an AM-type P state with $R(k) = 1$ it is $\frac{64}{13}$, and this ratio is likely to be far less sensitive to the precise form of $R(k)$ than the absolute magnitude of $\nu_L^2 - \nu_S^2$.

Precise Measurement of Effective Mass of Positive and Negative Charge Carriers in Liquid Helium II

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(Received 18 September 1972)

The resonance of charge carriers trapped under the surface of He II is observed at 200 MHz. The effective masses are found to be $m_+^* = (45 \pm 2)m_4$ and $m_-^* = (76 \pm 2)m_4$, where m_4 is a bare ^{4}He mass. The ionic radii are deduced to be $R_+ = 6.0 \pm 0.1$ Å and $R_- = 11.4 \pm 0.1$ Å.

We have used a resonance technique capable of an accuracy of better than 1% to measure the effective masses of negative and positive ions in liquid He II at temperatures below 0.8 K. The results are consistent with the bubble[1] and snowball[2] models for these ions, although the radius deduced for negative ions is rather low compared with other estimates. The technique is complementary to that of Dahm and Sanders[3] as it depends on having a very narrow-frequency response function for the electric susceptibility, whereas theirs requires a very broad response (they made a radiofrequency loss measurement far in the tail of the response function).

Ions can be trapped beneath a surface of He II by the combination of their image force and an electric field E applied perpendicular to the surface.[4] If x is the distance below the surface and ϵ the dielectric constant of the liquid, the potential may be written

$$V(x) = A/x + eEx, \quad A = e^2(\epsilon - 1)/4\epsilon(\epsilon + 1). \tag{1}$$

At sufficiently low temperatures the ion vibrates about the potential minimum with a frequency ω_0 determined by the second derivative,

$$\omega_0^2 = 2(eE)^{3/2}/m^* A^{1/2}, \tag{2}$$

where m^* is the effective mass for oscillatory motion of the ion in the liquid. Figure 1, appropriate to the positive ion, illustrates the orders of magnitude. The sharpness of the resonance is determined by $\omega_0\tau$, where τ is the momentum relaxation time; from the known mobilities[5] we see that, for $\omega_0/2\pi = 200$ MHz, $\omega_0\tau > 3$ below 0.9 K for both signs of ion and can reach $\omega_0\tau > 100$ below 0.6 K. The experiment consists in finding the applied field E at which the system resonates with an exciting x-directed radio-frequency field of about 200 MHz. As ϵ is known to good precision,[6] the relation (2) determines m^* directly. This method, which has also been proposed by Shikin,[7] permits a very precise measurement of m^* when $\omega_0\tau \gg 1$.

We measure the absorption as a function of E with a 200-MHz superheterodyne spectrometer[8]