Hysteretic Solidification of Surface ^{4}He Measured by the Modification of the Specularity of ^{3}He

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We have measured the superfluid fraction of ^{3}He in pores of sintered silver. The superfluid fraction, which is suppressed by confinement, increases with pressure due to the decreasing coherence length. Coating the surfaces with a thin film of ^{4}He partially restores the suppressed superfluidity, but above 17 bars this effect diminishes as the ^{4}He film solidifies. This solidification occurs over a range of about 9 bars and is hysteretic. With a slightly thicker ^{4}He film, solidification occurs at pressures greater than that required for bulk (25 bars).

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This Letter describes a series of experiments on ^{4}He and ^{3}He confined within the pores of sintered silver. The ^{3}He functions as both a hydrostatic medium to generate pressure as well as a detector of specular scattering of ^{3}He quasiparticles at the surfaces. The ^{4}He, which is preferentially plated onto the surfaces, serves as the agent to induce specularity as well as the material whose solidification is studied in this experiment.

The breaking of superfluid pairs of ^{3}He by a diffusely scattering surface produces a reduction in superfluid density and transition temperature which were predicted [1,2] and observed in a number of experiments [3-8]. Freeman *et al.* [7] observed that the transition temperature and superfluid fraction were restored to bulk values by the addition of ^{4}He, as is expected for a specularly scattering surface. Kim *et al.* [8] also saw an increase in the superfluid fraction of ^{3}He in a porous medium formed from μm-sized particles following the addition of ^{4}He. In the normal fluid, Tholen and Parpia [9] induced slip, which is associated with specular scattering, by the addition of similar coverages of ^{4}He to the surfaces.

One of the outstanding questions is whether the conversion of the ^{4}He fluid layer to a solid reduces the specularity. We find that solidification does destroy the specularity of the interface, and this destruction of specularity is used in this experiment to indicate the phase of the surface ^{4}He. The process of solidification occurs over a range of pressures starting below 25 bars, and is strongly dependent on the ^{4}He film thickness.

In this experiment, the ^{3}He was confined in a region with pore sizes comparable to the coherence length in the superfluid. The expected diffuse scattering of ^{3}He should break pairs and suppress the total superfluid fraction below the bulk value. Specular scattering induced by a surface layer of ^{4}He is expected to reduce or eliminate this suppression. By measuring the superfluid fraction following a change in pressure, we can determine the dependence of the specularity on the phase of the ^{4}He surface layer.

The experiments were carried out in a torsion oscillator cell which contained a 0.75-cm-diam 0.75-cm-tall cylindrical plug of silver powder (nominal diameter of 700 Å) sintered to 68% of solid density, with a 0.75-mm-diam hole drilled down the length of the sinter to promote thermal equilibrium. The cell was located in close proximity to an LCMN (lanthanum-diluted cerium magnesium nitrate) thermometer. The total surface area of the sample volume (measured using a standard technique [10]) consisted of 26.0 m^2 from the sintered heat exchanger which coupled the ^{3}He to the PrNi$_5$ nuclear refrigerator, plus 2.1 m^2 from the sintered silver itself. A melting curve thermometer was anchored to the body of the heat exchanger [11].

The superfluid fraction can be determined by measuring the shift in the resonant period of the oscillator. The empty cell period P_0 is determined by plotting the period at the transition temperature, $P(T_c)$, against the density and extrapolating to zero. At T_c, all the fluid contributes to the moment of inertia of the cell. The superfluid fraction can therefore be found from the relation

$$\frac{\rho_s}{\rho}(T)=\frac{1}{1-\chi}\frac{P(T_c)-P(T)}{P(T_c)-P_0}.$$

Here, χ is the fraction of the superfluid which contributes to the moment of inertia because of the tortuosity of the sinter. We find χ to be 0.68 from measurements on pure ^{4}He.

The zero-temperature coherence length of superfluid ^{3}He is given by the relation [12]

$$\xi_0=0.18\hbar v_F/k_BT_c.$$

For ^{3}He, this varies from $\sim$800 Å at 0 bar to $\sim$180 Å at 29 bars. In this sinter, the average pore size is approximately 2000 Å. Since the suppression of superfluidity occurs within about one coherence length of a diffusely scattering surface, the superfluid density is expected to be very small at low pressures, but should increase dramatically with pressure due to the rapid decrease of the coherence length.

The values for ρ_s/ρ at 17 bars are plotted in Fig. 1 for both pure ^{3}He and the lowest coverage ($\sim$3.5 monolayers) of surface ^{4}He. The superfluid density is clearly enhanced by the presence of the ^{4}He, though not restored to the bulk value [13]. Further, the suppression of T_c observed in the pure ^{3}He sample is no longer present after the addition of ^{4}He. The superfluid fraction is found to increase by $\sim$65% at $0.4T_c$ for all pressures at or below 17 bars.

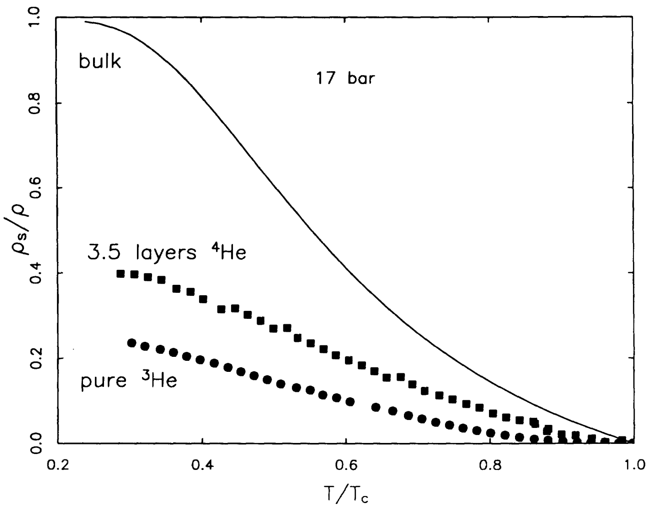

FIG. 1. Superfluid density as a function of T/T_c at 17 bars, with data shown for the pure ^{3}He sample as well as for the lower coverage of ^{4}He. The data for the 4.5-layer ^{4}He film is very similar to that for the 3.5-layer-thick film shown here. The solid line is the superfluid density for bulk ^{3}He.

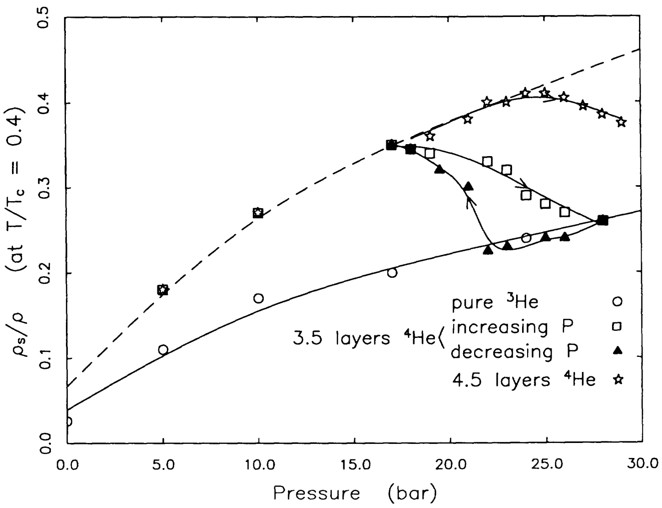

FIG. 2. Superfluid density at $T/T_c=0.4$ for various pressures. Open circles refer to the pure ^{3}He data (with the solid line through them serving as a guide), while the open squares and solid triangles are for the thinner ^{4}He coverage on increasing and decreasing pressure, respectively. The dashed line (specular scattering curve) is 1.65× the line through the pure ^{3}He result (see text). The stars refer to the thicker ^{4}He film.

The addition of ^{4}He introduces specularity only for coverages [7] greater than about 30 μmol/m^2, and is nearly complete [9] for 50–60 μmol/m^2. We started by adding 50 μmol/m^2 of ^{4}He, or approximately 3.5 monolayers. At this coverage, the surface scattering of ^{3}He quasiparticles is expected to be quite specular [9]. For flat surfaces, completely specular scattering should restore the superfluid fraction to that of the bulk [7]. However, the large mesoscopic curvature of our substrate requires bending terms in the order parameter which should suppress the superfluidity even in the presence of specular scattering [14].

We carried out a series of temperature sweeps for pure ^{3}He similar to those illustrated in Fig. 1. We plot the superfluid fraction in Fig. 2 at a reduced temperature of $T/T_c=0.4$ since this temperature is accessible at all pressures and ^{4}He coverages. At such a low reduced temperature, the superfluid fraction in the bulk liquid is close to unity [13] (see Fig. 1). The coherence length should be near its zero-temperature value, and effects due to suppression of T_c should be minimized. The superfluid density is clearly reduced for all pressures, with the amount of suppression decreasing as pressure increases (and coherence length decreases). As expected for diffusely scattering surfaces, the T_c's for the various pressures are also reduced. Because of the range of pore sizes and the effects of mesoscopic curvature, it is difficult to make comparisons between the suppression of ρ_s and T_c observed in this experiment with theory [15]. The general behavior, however, conforms well with expectations. This Letter will instead focus on the changes brought about by the addition of ^{4}He to the surfaces and its solidification.

As can be seen in Fig. 1, the suppression of ρ_s was substantially reduced upon the addition of ^{4}He. The solidification region above 17 bars will be discussed in greater detail later. Since the T_c was restored to its bulk value, we believe that the specularity of the surface is high, in agreement with our earlier measurements in the normal fluid. The fact that we do not see any further increase in the superfluid fraction with additional ^{4}He (to be discussed later), along with the results for specularity in the normal fluid [9], favors the argument that the fraction of specular scattering is nearly unity. As the pressure increases, the superfluid fraction is expected to continue to increase in the same proportion as was observed below 17 bars. This is illustrated in Fig. 2 by the dashed line.

Above about 17 bars, the enhancement of ρ_s begins to fall off with increasing pressure. As can be seen from Fig. 2, the transition from the specular scattering regime (dashed line) to the diffuse scattering regime (solid line) occurs over a broad pressure range. Once the pressure is above about 26 bars, the data for ρ_s/ρ at $0.4T_c$ with surface ^{4}He has reverted to the curve for pure ^{3}He.

Having attained a pressure of 28 bars (at which point the measured value of ρ_s was the same as that for the pure ^{3}He), we decreased the pressure. We found that ρ_s did not reproduce the path observed during pressurization [16]. Instead, the superfluid fraction decreased slightly, following the curve for the pure ^{3}He sample. At a pressure of 22 bars, ρ_s increased sharply before coinciding with the value obtained while increasing the pressure. Figure 3 shows an enlargement of the hysteretic region, with the dashed line representing the results of pressurizing to 24 bars and then decreasing pressure. We have reproduced this hysteresis loop twice in its entirety with

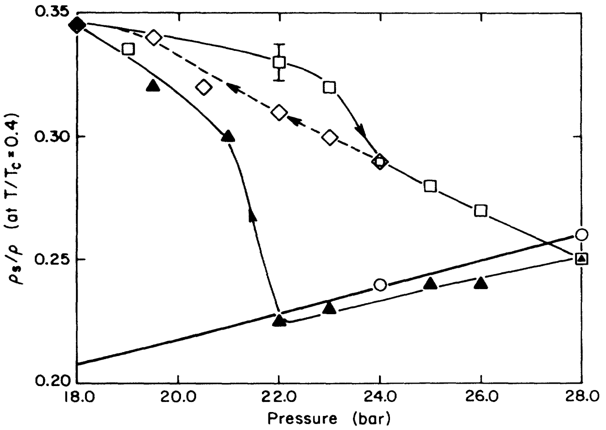

FIG. 3. Enlarged view of solidification region for the thinner ^{4}He film. The heavy solid line is the data for pure ^{3}He, or diffuse scattering. The solid lines show the region of hysteresis with the arrows indicating increasing or decreasing pressure. The dashed line and open diamonds are the data taken upon reducing the pressure from 24 bars. The other symbols are the same as in Fig. 2.

no significant deviations.

In order to explore this phenomenon further, we increased the coverage of ^{4}He to 65 μmol/m^2, or roughly 4.5 monolayers. We found no measurable change in the superfluid fraction at this higher coverage for pressures below 17 bars. However, the response of this film to higher pressures was dramatically different. At 17 bars, ρ_s/ρ continued to increase along the curve for specular scattering (dashed line in Fig. 2) instead of reverting to the pure ^{3}He, or diffuse scattering, curve. The increase continued until approximately 25 bars. From about 26 to 29 bars, the superfluid density dropped, although not to the diffuse-scattering value. This data set is indicated in Fig. 2 by the open stars. The pressure could not be raised further because of solidification of ^{3}He in the fill line.

We interpret the restoration of the superfluid fraction to the pure ^{3}He value as the result of solidification of the surface ^{4}He at high pressures. If this effect was due to the introduction of ^{3}He into the ^{4}He, then it should have been reversible. We do not believe there is any evidence that ^{3}He is present in the surface ^{4}He layer. Measurements of third sound [17] in ^{3}He/^{4}He mixture films a few monolayers thick are consistent with a simple model of nearly complete phase separation. The fact that we observed a monotonic increase of the specularity with the addition of ^{4}He (up to approximately 120 μmol/m^2) in our experiment in the normal fluid [9] (at 0 bar) also suggests that ^{3}He does not dissolve into the surface ^{4}He, since the ^{3}He would couple momentum across the intervening superfluid layer and decrease the slip. Thus, we assume that the decrease in the superfluid fraction indicates partial solidification of the surface ^{4}He. As we outline below, the hysteresis is consistent with a model of solidification at sites of higher local van der Waals potentials.

The model used by Landau and Saam [18] to describe the nucleation of solid ^{4}He assumes a local ^{4}He number density which depends on position. The number density is increased inside the attractive well created by the van der Waals potential of the substrate, increasing the local pressure at the substrate compared to the bulk. Solidification of a thin surface ^{4}He film should thus occur at a lower pressure than in the bulk.

However, when ^{4}He liquid fills the channels of a porous material, other factors may dominate. A model proposed by Dash [19] for ^{4}He solidification suggests that on disordered surfaces, the existence of grain boundaries in the solid ^{4}He at the surface increases the solid-substrate free energy, which in turn increases the pressure required to nucleate solid ^{4}He. The amount of overpressure is determined by the volume-to-surface-area ratio as well as the surface roughness and geometry. Alternatively, Lie-zhao *et al.* [20] propose that ^{4}He liquid contained in a porous geometry might nucleate within the small fluid region of the pores rather than on the substrate surfaces. In this case, the work needed to form a nucleus provides a potential barrier against formation of the solid. The nucleus is stabilized by an excess pressure, proportional to the interfacial tension between liquid and solid. Although the mechanisms are different, both these models [19,20] predict that excess pressure will be required to solidify ^{4}He in a disordered medium and compete with the mechanism described by Landau and Saam [18].

Previous experiments have measured ^{4}He solidification only in systems of pure ^{4}He, in contrast to our arrangement in which a thin film of ^{4}He in a porous geometry is covered by ^{3}He. Lie-zhao *et al.* [20] found that for ^{4}He in Vycor (with average pore size of $\sim$70 Å), superfluidity was still present at pressures as much as 20 bars above bulk solidification. Similar experiments using various pore sizes [20,21] also found an increased solidification pressure, with higher pressures required for the smallest pore sizes. We also note that layered solidification was observed on graphite [22], which is wetted by ^{4}He, at pressures well below the bulk solidification pressure. In all of these experiments, the amount of ^{4}He in contact with the substrate was only a small fraction of the total ^{4}He sample. For our experiment, however, the amount of ^{4}He was fixed and confined to the surfaces; thus, our experiment directly samples surface solidification.

The superfluid transition temperatures of a 90-μmol/m^2-thick ^{4}He film covered by bulk ^{3}He on a flat Mylar substrate were measured as a function of pressure [23]. Transitions continued to be observed above the bulk solidification pressure up to 29 bars, indicating that liquid was still present. This agrees with our current results which indicate an increased pressure required for solidification of a "thick" ^{4}He film covered by ^{3}He.

Solidification of our thinner ^{4}He layer occurred substantially *below* the bulk solidification pressure for ^{4}He (25 bars) and was strongly hysteretic. The range of pressures over which solidification was observed is thought to result from the presence of sites with varying strengths of local van der Waals potential. In a more uniform surface geometry, solidification would presumably occur more abruptly. Thus, for this film thickness, the mechanism proposed by Landau and Saam dominates the solidification. Complete solidification was not possible for the thicker ^{4}He film. However, solidification commences near 25 bars and is not complete at 29 bars. For this film thickness, the van der Waals contribution from the substrate is less important than the mechanisms that lead to the elevation of the melting pressure in the full-pore experiments. Clearly, the various contributions to solidification are comparable and we have been able to observe both regimes in a single experiment.

The fact that we have been able to observe the solidification of the thinner ^{4}He films at reduced pressure (from bulk) indicates that the solid nucleates at the surfaces. This seems to favor the description by Dash to explain the overpressure required to solidify thicker ^{4}He films. As the film thickness is increased and additional solid nucleates onto the surface solid layer, the grain-boundary energy of ^{4}He crystallites becomes more important. Since there are no bulklike fluid regions in the films, the model of Lie-zhao *et al.* is probably not applicable to our system.

Interactions between solid regions nucleated at different sites result in hysteresis. The solid grows outward from regions of higher potential, and as pressure increases, some regions coalesce to form larger plates of solid. These regions, having a smaller ratio of surface area to volume, are stable at lower pressures. Thus, once all the ^{4}He film has solidified, it is stable at a lower pressure than was required to solidify it. This picture would give rise to hysteresis even for incomplete solidification, as we observed upon reducing the pressure from 24 bars (Fig. 3, dashed line). Alternatively, providing the model of Dash is applicable, an additional mechanism for hysteresis via the annealing of grain boundaries may be relevant.

To summarize, we have seen that solidification of surface ^{4}He films leads to a destruction of specular scattering of the ^{3}He quasiparticles from the surfaces. Solidification of the surface ^{4}He for our thinnest films occurs at a pressure below that of bulk, in accord with the theoretical expectation of Landau and Saam. The increase in solidification pressure for our thicker film is in qualitative agreement with that observed in earlier full-pore experiments. The hysteretic behavior indicates that the solid preferentially nucleates at sites of stronger van der Waals potentials. Finally, the technique of observing solidification of thin ^{4}He films using ^{3}He as a hydrostatic medium should be a useful tool for the investigation of ^{4}He interactions with various substrates.

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[1] V. Ambegaokar, P. G. de Gennes, and D. Rainer, Phys. Rev. A **9**, 2676 (1974).

[2] L. H. Kjäldman, J. Kurkijärvi, and D. Rainer, J. Low Temp. Phys. **33**, 577 (1978).

[3] M. T. Manninen and J. P. Pekola, J. Low Temp. Phys. **52**, 497 (1983).

[4] V. Kotsubo *et al.*, Jpn. J. Appl. Phys. **26**, 143 (1987).

[5] V. Kotsubo, K. D. Hahn, and J. M. Parpia, Phys. Rev. Lett. **58**, 804 (1987).

[6] T. Chainer, Y. Morii, and H. Kojima, J. Low Temp. Phys. **55**, 353 (1984).

[7] M. R. Freeman *et al.*, Phys. Rev. Lett. **60**, 596 (1988); M. R. Freeman and R. C. Richardson, Phys. Rev. B **41**, 1101 (1990).

[8] D. Kim *et al.*, Physica (Amsterdam) **165&166B**, 637 (1990).

[9] S. M. Tholen and J. M. Parpia, Phys. Rev. Lett. **67**, 334 (1991).

[10] S. Brunauer, P. H. Emmett, and E. Teller, J. Am. Chem. Soc. **60**, 309 (1938).

[11] J. M. Parpia *et al.*, Rev. Sci. Instrum. **56**, 437 (1985).

[12] P. G. de Gennes, *Superconductivity of Metals and Alloys* (Benjamin, New York, 1966).

[13] J. M. Parpia *et al.*, J. Low Temp. Phys. **61**, 337 (1985).

[14] E. Thuneberg (private communication).

[15] K. Ichikawa *et al.*, Phys. Rev. Lett. **58**, 1949 (1987).

[16] The pressure was changed by bleeding ^{3}He into or out of the cell holding $T < 5$ mK. Typical pressure steps while traversing the hysteresis loop were 1 bar. The experiment was not warmed above 50 mK during precool.

[17] F. M. Ellis *et al.*, Phys. Rev. Lett. **46**, 1461 (1981).

[18] J. Landau and W. F. Saam, Phys. Rev. Lett. **38**, 23 (1977).

[19] J. G. Dash, Phys. Rev. B **25**, 508 (1982).

[20] C. Lie-zhao *et al.*, Phys. Rev. B **33**, 106 (1986).

[21] E. D. Adams *et al.*, Phys. Rev. Lett. **52**, 2249 (1984).

[22] V. Gridin *et al.*, Phys. Rev. Lett. **53**, 802 (1984).

[23] M. Freeman, Ph.D. thesis, Cornell University, 1988 (unpublished).