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Phase transition of two-dimensional ^{3}He from a dilute to a dense phase

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We have measured the heat capacity of ^{3}He in films of ^{4}He as thin as 10 Å formed on a Nuclepore filter substrate. At low temperatures, where the ^{3}He is in the lowest state as far as motion perpendicular to the film surface, we find that the ^{3}He undergoes a transition from a dilute phase to a dense phase. We have observed this transition for films of ^{4}He of 12.3- and 10-Å thickness and for coverages of ^{3}He below about 0.2 atomic layers. For thicker ^{4}He films, and higher ^{3}He coverages, the ^{3}He remains homogeneously spread out over the surface of the ^{4}He. The striking characteristic of the transition is the sudden onset of linear temperature dependence with a slope which is proportional to the amount of ^{3}He in the calorimeter. This is consistent with the formation of islands of a dense two-dimensional phase which grows in extent proportionately to the amount of ^{3}He. Two puzzling aspects of our results are the lack of a significant heat-capacity jump at the transition and, based on a linear extrapolation of the data to zero temperature, a substantial amount of missing entropy.

I. INTRODUCTION

The ability of ^{4}He to form relatively thick films at low temperatures on all surfaces exposed to it has allowed one to observe a multitude of phenomena, ranging from the modification of critical behavior to the modification of the low-temperature superfluid properties. All of these aspects can be studied as a function of the thickness of the ^{4}He, thus allowing one to observe effects in the strictly two-dimensional (2D) regime, as well as in the 3D to 2D crossover regime. This has been especially useful in the study of critical behavior near the superfluid transition. The character of this transition changes dramatically in two versus three dimensions.

The addition of ^{3}He to films of ^{4}He allows one to study not only the very same phenomena which occur in pure ^{4}He and are now modified by the ^{3}He impurity, but also some rather different phenomena. Among these new phenomena is the two-dimensional ^{3}He layer which forms at the liquid-^{4}He-vacuum interface.[1] This "surface" ^{3}He was first realized in the case of the bulk ^{4}He surface. A single atom of ^{3}He prefers the low-density environment of the vacuum-liquid interface versus solution in the ^{4}He, because the cost in the kinetic energy of confinement within the ^{4}He is too high relative to the gain in potential energy. This surface occupation or adsorption can be realized up to a density of about 6.4×10^{14} cm^{-2}. At this point, the Fermi energy becomes very nearly equal to the surface binding energy and the ^{3}He begins to dissolve within the ^{4}He. The behavior of this 2D ^{3}He at the bulk surface has proved to be that of an ideal gas of Fermi quasiparticles bound at the surface with an energy of 2.2 K, and having an effective mass of 1.45 ^{3}He atomic masses. One of the early conjectures for this ^{3}He was a possible condensation into a liquid state.[2] This has not yet been observed.

The situation where the ^{3}He is adsorbed on the surface of films of ^{4}He, as opposed to that of bulk ^{4}He, can be expected to be rather different. The native excitations of the ^{4}He are substantially modified in a film geometry.[3] Furthermore, the density environment at the free surface is affected by the additional van der Waals field produced by the solid substrate upon which the film is formed. Last, but not least, is the fact that the excited states for the ^{3}He in a film are not a 3D continuum, but rather, discrete subbands, the energy of which depends on the thickness of the ^{4}He.[4,5] In earlier publications, we have reported measurements of the heat capacity of ^{3}He in films of ^{4}He, where the ^{3}He behaves as a 2D Fermi gas of uniform density.[5] The analysis of these data yields information on the ^{3}He effective mass and the excitation energy to higher states. We have also reported in a previous paper[6] that at low ^{3}He density on a 12.3-Å film of ^{4}He, we have observed a sudden transition of the ^{3}He from a dilute, uniform density phase, into a denser, degenerate phase. In this paper, we report additional data for ^{3}He on a 10-Å ^{4}He film which also shows this transition, and we discuss this observation in more detail. Much of the groundwork for this paper has been done in two earlier publications. Bhattacharyya, DiPirro, and Gasparini (BDG) discuss the data where the ^{3}He remains homogeneously spread out over the surface of the film.[5] The parameters of the energy states and the effective masses, and the dependence of these on coverage, are discussed in this work. In another publication, Gasparini, Bhattacharyya, and DiPirro presented a variational theory for the binding of ^{3}He to the film of ^{4}He.[7] This has also been done and extended by Sherrill and Edwards.[8] This single-particle theory is perhaps applicable in the limit of zero ^{3}He coverage, but has served as a model for the data analysis of ^{3}He at nonzero coverages. Recently a variational theory has also been proposed by Krotscheck for films of ^{4}He formed on an idealized graphite substrate.[9] This theory has also been used to calculate the binding of ^{3}He to the ^{4}He.

II. EXPERIMENTAL DETAILS

The films of ^{4}He we study are formed on the surface of Nuclepore filters. Specifically, 2000 filters having pores of 2000-Å nominal diameter and at a density of 3×10^8 cm^{-2} are used to yield a surface area of about 10^6 cm^2. This area is measured by nitrogen adsorption.[10] The heat capacity of films ranging in thickness from 10 to about 45 Å above a 3-Å solid layer have been studied. Coverages of ^{3}He in the range of $\sim$0.01 to 1 layer have been measured. The layer designation is in units of 6.4×10^{14} cm^{-2}, a number which is the $\frac{2}{3}$ power of the ^{3}He bulk density at zero pressure. In temperature, the data extend from 40 to 750 mK. The points in the (^{4}He thickness)—(^{3}He coverage) plane where data have been taken are shown in BDG. We also refer to this publication for further details regarding the calorimeter, thermometry, and the procedure of data taking.

III. EXPERIMENTAL RESULTS

In Fig. 1, we show the low-temperature part of the heat-capacity data for ^{3}He coverages of 0.048 to 0.293 layers on a 10-Å ^{4}He film.[11] These data actually extend to higher temperatures, $T\cong0.7$ K, and the solid lines through these data are the results of fitting the data to a model where the ^{3}He behaves as a 2D gas of Fermi quasiparticles. In addition to the 2D degrees of freedom, the ^{3}He can be promoted to excited states within the film, and, at higher temperatures, into the vacuum. This is the reason the data shown in Fig. 1 rise above the 2D Boltzmann value, N_3k_B, indicated by the dashed lines on the ordinate. The details of the model used in this analysis are given in BDG. For the two highest coverages shown in Fig. 1, the solid lines extend down to the lowest temperature where we have data. These lines extrapolate to the origin in a linear fashion, as expected for a degenerate Fermi system. The slight difference in the slopes for these coverages is attributed to variations in the effective mass, m. For a 2D Fermi system, the heat capacity C is given by

$$C=\frac{\pi k_B^2}{3\hbar^2}mAT\ , \qquad (1)$$

where A is the area. Thus, in two dimensions, unlike in three, the heat capacity is independent of density. For our data, then, apart from variations in the effective mass, we would expect the same low-temperature slope. We see, on the contrary, that the lowest-coverage data display quite a different behavior. In the neighborhood of 100 mK, the data break off from what is very nearly the Boltzmann value to a linear T dependence. This sudden onset of degeneracy is suggestive of the formation of a dense phase for the ^{3}He. Since such a phase would occupy a subset of the total area, then, on the basis of Eq. (1), one would have a lower slope for the heat capacity. We first suggested this mechanism based on measurements of heat capacity for ^{3}He on a 12.3-Å ^{4}He film.[6,12] Some of these data are shown in Fig. 2. Here, we see that at the two lowest coverages, we measure just the expected Boltzmann value, the solid lines. The Fermi temperatures for these two coverages are well below the range of these data, 0.002 and 0.04 K, respectively. Promotion of the ^{3}He to excited states is also negligible at these temperatures and coverages. At the next higher coverage shown in this figure, a behavior very similar to that observed in Fig. 1 is obtained, a sudden break of the data into very nearly a linear T dependence. A similar situation also occurs at a coverage of 0.092 layers, but this is now accompanied by a slight jump in the heat capacity. The expected temperature dependence, if the ^{3}He behaved as an ideal 2D gas of quasiparticles spread out over the surface of the ^{4}He film, is indicated for the 0.058-layer data as the solid line extending to the origin.

A simple test to check that the data shown in Figs. 1 and 2 represent the formation of a dense phase is the fact that in this circumstance, the slope of the low-temperature part of data should be proportional to the number of ^{3}He atoms in the calorimeter. We indicate this schematically in Fig. 3. Here, we picture the new phase as "islands" where the density of ^{3}He is higher. As more atoms are added to the calorimeter, the area occupied by these islands increases. Thus, as expected from Eq. (1), so does

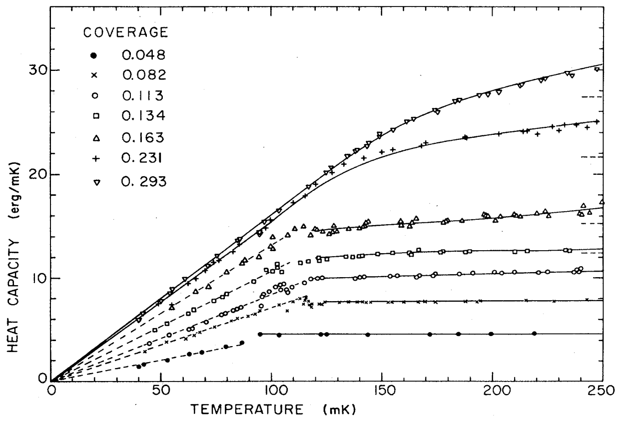

FIG. 1. Heat capacity of ^{3}He at various coverages on a 10-Å ^{4}He film. The solid lines represent a fit of the data under the assumption that the ^{3}He is homogeneously spread out over the surface of the film. The dashed lines are drawn to guide the eye.

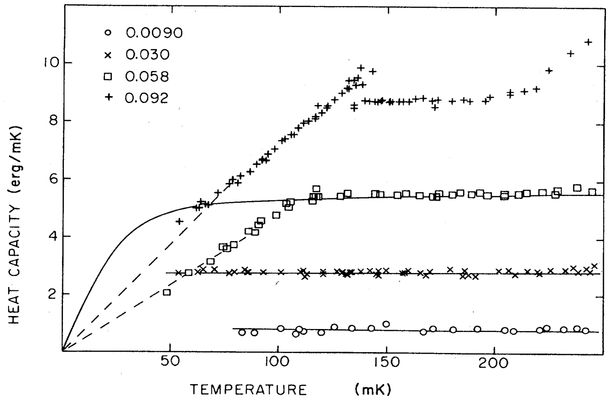

FIG. 2. Heat capacity of ^{3}He at various coverages on a 12.3-Å ^{4}He film. The solid lines through the two lowest coverages are drawn at the expected Boltzmann value. The solid line through the squares is the expected behavior of the data if the ^{3}He were to remain homogeneously spread out over the ^{4}He film. The dashed lines are drawn to guide the eye.

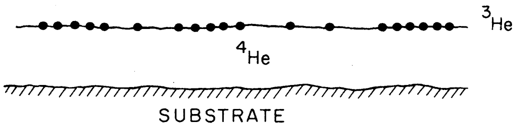

FIG. 3. Schematic representation of 2D-phase separated ^{3}He on the surface of a ^{4}He film.

the low-temperature slope. A quantitative check on this behavior is shown in Fig. 4. Here, we have plotted the low-temperature slope as a function of the number of ^{3}He atoms in units of coverage. We see that the eight lowest coverages on the 10-Å ^{4}He film fall very nicely on a straight line going through the origin. This supports the assertion of the growth in the area of the condensed phase with addition of ^{3}He. For the 12.3-Å data, the two lowest coverages also fall on the same straight line, but at higher coverages (some of these data were shown in Ref. 6), there are deviations. One does, of course, expect deviations since eventually, at higher coverages, no transition is observed. In this case then, the slope must go to a value which is very nearly constant, apart from small variations in the effective mass. The expected low-temperature slope for a representative effective mass, $m = 1.7m_3$, is given by the horizontal dashed-dotted line in Fig. 4.

It might also appear that the heat capacity, being proportional to the number of atoms, could also be an indication of the formation of a three-dimensional "bubble" of ^{3}He. In this case, in the degenerate regime, one has

$$C=\frac{\pi^2 k_B^2 m}{\hbar^2}\left[\frac{V}{3\pi^2 N}\right]^{2/3} NT \qquad (2)$$

with V/N the density and N the total number of atoms. We have calculated the slope by using $m = 2.76m_3$ and $V/N = 36.8$ cm^3/mole, values attained for bulk ^{3}He at zero pressure. We find that the slope given by Eq. (2) is about 3.5 times smaller than the experimental results. To agree with experiment, the bubble's molar volume would have to be 6.6 times larger. This, in turn, would suggest yet a lower value of m, which would lower the calculated slope even further. Thus, it seems that a 3D bubble is not a likely candidate for the low-temperature dense phase.

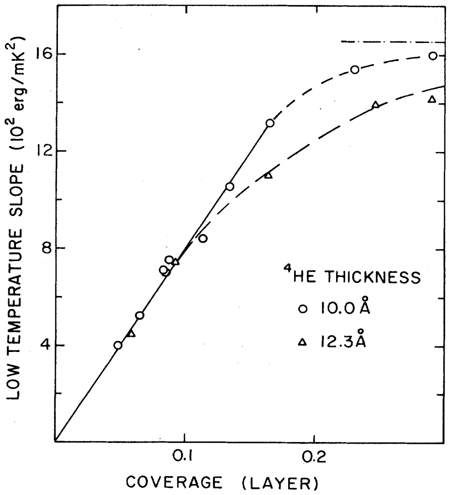

FIG. 4. Low-temperature slope of the heat capacity at various coverages and for two ^{4}He film thicknesses. The dashed-dotted line is the slope that all the data should have, if the ^{3}He were homogeneously spread out over the ^{4}He film surface. We have used an effective mass of $1.7m_3$ for this line.

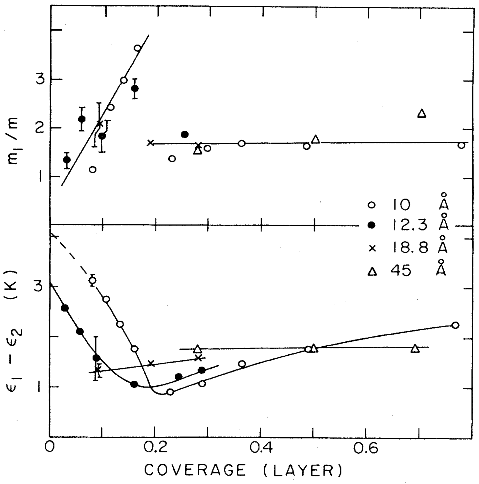

FIG. 5. Behavior of the effective mass and the excitation energy as function of coverage for various ^{4}he films. The data which show the low-temperature transition have a minimum in the excitation energy and a rather marked dependence of the effective mass on coverage. The solid lines are drawn to guide the eye.

There are two other interesting features of the data which display the transition in Figs. 1 and 2. These come from the analysis of the high-temperature part of these data where the ^{3}He is homogeneously spread out over the surface of the film. These features were first pointed out by BDG, and are reproduced in Fig. 5. Here, we have plotted as a function of coverage the effective mass and the energy to excite the ^{3}He from the ground state to the first excited state. In the case of the effective mass we notice, at low coverages, a strong, nearly linear dependence on coverage up to about 0.2 layers. Beyond this value, and these are the data for which no transition is observed, the effective mass does not vary appreciably. In the lower part of Fig. 5, we show the excitation energy as a function of coverage. Interestingly, the data for the thinnest ^{4}He films where the transition is observed, show a minimum as a function of coverage. The data for films of ^{4}He of 18.8 and 45 Å do show a coverage dependence, but no minimum. No transition is observed for these thicker films at any coverage, at least down to temperatures of ~0.05 K.

IV. COMMENTS AND DISCUSSION

We have presented in the preceding section experimental results which can be interpreted as evidence for the formation of a two-dimensional dense phase for ^{3}He on thin films of ^{4}He. There are, however, some important aspects of these data which remain a puzzle. These are the lack of evidence for a "gas" phase in equilibrium with the condensed phase, the lack of an appreciable jump in the heat capacity at the transition, and, perhaps related to both of these aspects, a substantial missing entropy.

Regarding the gas phase, one would expect that upon phase separation, or the formation of a 2D liquid, there would be in equilibrium with it a dilute phase. We have tried to indicate this in Fig. 2 with a few atoms between the islands of dense phase. The presence of the dilute phase should add to the low-temperature heat capacity, which would be enhanced above a linear T dependence. To some extent, we have seen this for the data on the 12.3-Å film, at least at higher coverages.[6] But the evidence is not conclusive. Certainly for the 10-Å film, as can be seen from Fig. 1, there seems to be no evidence at any coverage of a dilute phase. The data fit very nicely on straight lines going through the origin.

Another feature which is missing from our data is an expected jump in the heat capacity at the transition. As one warms up from the inhomogeneous phase to the homogeneous phase, the heat capacity should have a downward jump. Although we cannot calculate this jump because of lack of thermodynamic information, the magnitude is related to the square of the reciprocal of the coexistence curve. We show in Fig. 6 the locus of points where we observe a break in our data. In the case of the 10-Å film, the coexistence curve is exceedingly flat. This would tend to enhance the magnitude of the expected jump.

Related to the jump feature is the missing entropy. In Fig. 2, we have emphasized, via the solid line through the 0.058-layer data, the expected low-temperature behavior of the heat capacity if the ^{3}He were to remain homogeneously spread out over the surface of the ^{4}He. It is clear from the difference between this line and the data for which it is calculated that a substantial amount of entropy is missing. In Fig. 7, we have plotted the entropy difference at the transition between the measured experimental path and a thermodynamic path where the ^{3}He remains homogeneous. The missing entropy seems to be nearly linear with coverage for the 10-Å film, but shows no particular dependence for the 12.3-Å film.

There are several possibilities to explain the missing entropy. It is possible that the linear extrapolation of the data to zero temperature used in calculating the experimental entropy is not valid because another transition intervenes. This obviously can only be checked by measurements at lower temperatures. Another possibility is that a very sharp peak exists at the transition which is not resolved in our measurements. This does not seem very likely since no evidence of a precursor is observed. In addition, the peak would have to be extremely high to account for the missing entropy, $\sim 200k_B$, for a 1-mK width.

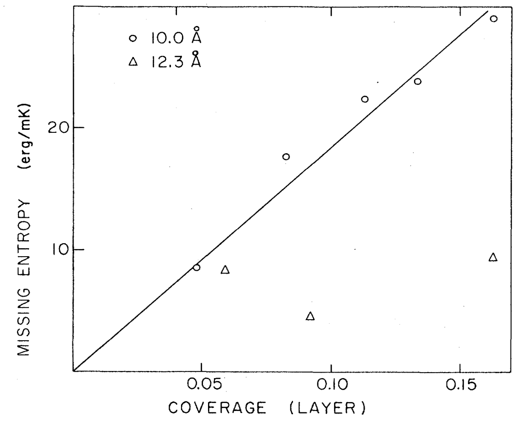

FIG. 7. Missing entropy as function of coverage for the data which display the low-temperature transition.

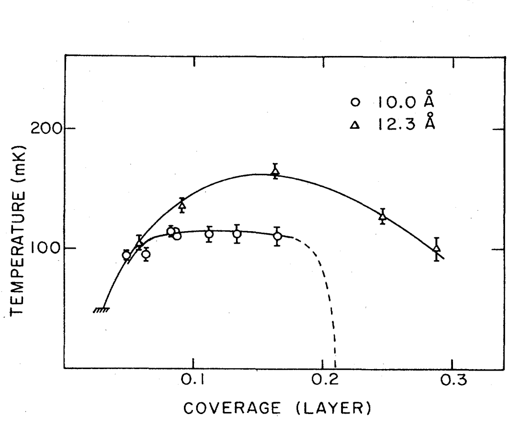

FIG. 6. Locus of points where we have observed the phase transition in the ^{3}He.

A third possibility is that below the transition, one has lost thermal contact with some of the ^{3}He. This possibility would be consistent with the low-temperature slopes being proportional to coverage only if one were to lose contact with a constant fraction of the ^{3}He at each coverage. If one were to lose contact with the same amount of ^{3}He, then the line in Fig. 4 would not go through the origin. To see if this is a possibility, we have assumed that the missing entropy is due to a dilute amount of ^{3}He spread out over some subset of the calorimeter area which is not occupied by the condensed phase. Since the missing entropy for the 10-Å film data is very nearly $2N_3k_B$, we have looked for a solution of the equation

$$2N_3k_B = N_m k_B \frac{T_c}{T_{Fm}}[2S_1(\eta_m) - \ln(\eta_m+1)\ln\eta_m] \ , \qquad (3)$$

where S_1 is defined in Ref. 13, N_m is the missing amount of ^{3}He with Fermi energy T_{Fm}, $\eta_m = \exp(T_{Fm}/T_c) - 1$, and T_c is the transition temperature. The right-hand side of Eq. (3) is the expression for the entropy of a 2D Fermi gas.[13] We find that the above equation has a solution for the lowest coverages only for values of η_m corresponding to N_m greater than the total amount condensed.[14] At the highest coverage, there is no N_m which satisfies this equation. Thus, a missing amount of ^{3}He acting as a 2D gas is not a viable explanation for the missing entropy.

A fourth possibility is that the low-temperature state we observe is really metastable; thus, consideration of missing entropy would not apply. In the case of the data for the 12.3-Å film, we have seen some evidence of metastability near the transition. A careful inspection of Fig. 2 shows that data from the low-temperature branch overlap the data above T_c. In the other coverages, however, especially those for the 10-Å film, we have seen no evidence of metastability. In particular, we note that most of the coverages represent the accumulation of several runs taken over a period of several weeks. These reproduce within the scatter of these measurements. We also note that all the data were taken starting at low temperature, i.e., in the condensed phase, and then warming through the transition. This, it would seem, would be the wrong direction for observing metastability in a process of phase separation.

In conclusion, then, it would seem that among the various possibilities we have considered for the missing entropy, the most likely ones are some additional structure in the heat capacity at lower temperatures or some peculiar metastability which causes our system not to be in thermodynamic equilibrium.

V. LOW-TEMPERATURE PHASE

While we have discussed the transition of the ^{3}He as a 2D phase separation or a gas to liquid transition, we emphasize that we do not really know the nature of the low-temperature phase. The experimental observation is that of a sudden onset of linear T dependence, which we interpret as the formation of a degenerate Fermi system. The slope of the low-temperature data being proportional to the amount of ^{3}He is consistent with the area occupied by the condensed phase simply increasing with coverage. That is, a constant density phase increasing in extent as more ^{3}He is added. Both of these possibilities, isotopic separation or gas-to-liquid transition, would be consistent with the data, and share the common difficulties discussed in the preceding section. Both of these possibilities have also been considered theoretically.[2,15] Phase separation is perhaps more appropriate for near monolayer mixture films of ^{3}He and ^{4}He where the ^{4}He plays a rather different role than in the case of a thicker film. In this latter case the ^{4}He provides principally a surface upon which the 2D ^{3}He is formed. In this case, a gas-to-liquid transition might perhaps be the more appropriate description.

Another possibility, suggested by several authors,[16] is that the 2D ^{3}He forms a diatomic molecule, or perhaps even a polymer. This would not seem to be consistent with our data. The formation of such a state proceeds in a continuous way and not as a sudden transition. Calculations of the heat capacity for values of the dimer binding energy in the range of 0.2—0.5 K yield results quite different from our measurements.

Yet another possibility one may consider is an inhomogeneity of binding sites on the ^{4}He film. These would have to be "extended" sites or regions where the ^{3}He would retain its 2D degrees of freedom so that the proper Boltzmann heat capacity, which we always measure, is retained. Upon cooling such a system, the ^{3}He would settle into the sites of greatest binding. Such a process occurs in a continuous, thermally activated way and not as a sudden transition. Furthermore, given that these greater binding regions take up a certain portion of the substrate, then the area occupied by the condensed ^{3}He would not be proportional to the amount of ^{3}He, but rather a characteristic number determined by the substrate. This, again, is contrary to our observations.

Recently, Guyer[17] has suggested that a possible mechanism for phase separation of 2D ^{3}He in films of ^{4}He results from the coupling of the ^{3}He coverage to the ^{4}He film thickness. In this theory the phase separation of the ^{3}He would occur simultaneously with a deformation of the ^{4}He thickness. The denser ^{3}He phase would reside on somewhat thicker film regions than the dilute phase. This picture is certainly consistent with our heat-capacity data. Our data, however, are not really sensitive to a small deformation of the ^{4}He film thickness, but rather only to the ^{3}He density, thus we cannot really verify this mechanism of thickness deformation. Another feature of this theory is that at high coverages of ^{3}He or thicker films of ^{4}He the transition would disappear. This is certainly consistent with our observations.

We finally point out that measurements of third sound[18] and superfluid mass[19] have been made of ^{3}He-^{4}He mixture films. The data do not overlap, however, the region of thickness—^{3}He coverage where we have observed the phenomena discussed in this paper. It is interesting to note, however, that these measurements have revealed other, in some cases, anomalous behavior, which at present is not understood. The likely picture which will emerge from all this work is that several regions of behavior exist. Understanding these observations will further extend our understanding of two-dimensional physics and quantum fluids in particular.

VI. SUMMARY AND CONCLUSIONS

We have presented evidence from measurements of heat capacity of ^{3}He in films of ^{4}He that, for a certain range of ^{3}He coverages and ^{4}He film thickness, the ^{3}He separates into a 2D dense phase. Features of this transition are a sudden onset of degeneracy with little evidence for an equilibrium dilute phase, a very small, if any, heat-capacity jump, and a rather large amount of missing entropy based on the extrapolation of the data to zero temperature. The formation of this dense phase may be viewed as an isotropic phase separation, a liquefaction, or a phase separation associated with the ^{4}He-thickness deformation. Our data cannot distinguish among these. The data do not agree with the formation of 3D bubbles of ^{3}He, a dimerization or polymerization of the ^{3}He, or a separation of the ^{3}He due to inhomogeneities of substrate binding sites.

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