a periodically modulated thickness.[13] Second-order commensurate/incommensurate transitions have been observed experimentally for molecules H_2 and D_2, atoms He^3 and Kr, and some others adsorbed on a Grafoil substrate.[9] Our theory cannot be applied directly to these cases because two pairs of basic reciprocal lattice vectors become close simultaneously. The appropriate calculations are now in progress.

We are indebted to P. B. Wiegmann for illuminating discussions and to A. I. Larkin who informed us that he and A. Luther came to the same model in connection with the problem of a vortex lattice in a superconducting film.[13]

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[1] See references 1–6 in V. L. Pokrovsky, Solid State Commun. 26, 77 (1978); see also O. Daldini, P. Martinoli, T. L. Olsen, and G. Berner, Phys. Rev. Lett. 32, 218 (1974).

[2] S. C. Ying, Phys. Rev. B 3, 4160 (1971).

[3] Pokrovsky, Ref. 1.

[4] V. L. Pokrovsky and G. V. Uimin, J. Phys. C 11, 3535 (1978).

[5] A. D. Novaco and J. P. McTague, Phys. Rev. Lett. 38, 1286 (1977).

[6] L. N. Bulayevsky and D. I. Khomsky, Zh. Eksp. Teor. 74, 1863 (1978).

[7] G. Theodorou and T. M. Rice, 1978 (to be published).

[8] V. L. Pokrovsky and A. L. Talapov, Zh. Eksp. Teor. Fiz. 75, 1151 (1978).

[9] L. A. Bolshov, A. P. Napartovich, A. G. Naumovetz, and A. G. Fedorus, Usp. Fiz. Nauk 122, 125 (1977) [Sov. Phys. Usp. 20, 432 (1977)]; M. Nielssen, W. D. Ellenson, and J. P. McTague, in *Proceedings of the International Symposium on Neutron Inelastic Scattering, Vienna, 1977* (International Atomic Energy Agency, Vienna, 1978), p. 433.

[10] P. B. Wiegmann, J. Phys. C 11, 1583 (1978).

[11] A. Luther and V. J. Emery, Phys. Rev. Lett. 33, 589 (1974).

[12] A. Luther and V. L. Pokrovsky, unpublished. The results are reproduced in Ref. 8.

[13] Daldini, Martinali, Olsen, and Berner, Ref. 1.

Absence of Substrate Nucleation for bcc Solid ^{3}He on Grafoil

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In contrast to the case of ^{4}He, we find no evidence for spontaneous nucleation of a uniform surface solid layer from the liquid phase of ^{3}He near Grafoil substrates. However, surface solid could be detected after forcing the rapid growth of bulk solid from external points of nucleation. The experiment covers the temperature range between 30 and 320 mK at pressures just below the bulk melting curve.

The role of a Grafoil substrate in nucleating solidification from superfluid ^{4}He was studied recently by Landau and Saam[1] (L-S). The principal conclusion was that uniform nucleation of a surface solid phase always occurs as the pressure approaches the bulk melting curve. If the general analysis of Dash[2] and Peierls[3] are applied to this problem, one concludes that the growth of the ^{4}He surface solid is analogous to their Class-I adsorption process (i.e., unimpeded growth of the adsorbed layer). The principal purpose of this experiment was to test whether the Class-I behavior also applied to nonsuperfluid ^{3}He on Grafoil. We found, to our surprise, that ^{3}He does not show any sign of uniform nucleation of a solid phase near the bulk melting curve. These results, combined with the observation from neutron diffraction studies[4-7] that the completed monolayer of noble gases, including ^{3}He and ^{4}He, adsorbed on Grafoil displays a triangular symmetry, suggest that continuous growth of a liquid-solid interface is possible only when the symmetry of the monolayer matches the symmetry of the bulk solid lattice. The hexagonal structure of solid ^{4}He matches with a triangular monolayer while the cubic structure of ^{3}He does not. Thus the adsorptive solidification of ^{3}He on Grafoil should be classified as Class II in the Dash-Peierls scheme.

In the L-S experiment the nucleation of solid ^{4}He layers on Grafoil in equilibrium with bulk superfluid ^{4}He was studied using equation-of-state–type measurements. They observed isopycnals[8] just below the bulk melting curve, finding that they differ appreciably from isochores of the bulk superfluid. This difference was explained via the uniform growth of solid layers over the entire Grafoil substrate to a thickness z_s due to the Grafoil-He substrate interaction. This van der Waals interaction causes He atoms near the substrate surface to be at much higher local pressures than those far away. The local pressure at a finite distance z from the substrate is given to a good approximation as

$$P(z) \simeq P(z=\infty) + \alpha n_L / z^3, \tag{1}$$

where n_L is the liquid number density and α is a constant. It was assumed that if $P(z)$ of the liquid is equal to or larger than the melting pressure then solid is formed. L-S constructed a quantitative theory giving the thickness of the surface solid layer as a function of the difference between the bulk pressure and the melting pressure at a given temperature. The agreement between this theory and the isopycnal experiment, checked at different densities, is reasonable.

In the present experiment we performed L-S-type measurements on the system of ^{3}He in contact with Grafoil, thereby extending our earlier, preliminary study of ^{3}He surface solid on activated charcoal,[9] as well as examining speculations suggested by Bukshpan *et al.*[10] and Brewer, Mitchell, and Truscott[11] *a priori*, one would expect to get the same results, qualitatively, as for ^{4}He; after all, the van der Waals forces are the same for both ^{3}He and ^{4}He. We found that under the many varied conditions that we tried, ^{3}He shows no nucleation of surface solid from the bulk liquid phase. The first indication of solid nucleation always turned out to be bulk solid, apparently external to the Grafoil pores.

The constant-volume experimental cell was made of copper and filled with Grafoil. The weight of the Grafoil was 3.86 g having a substrate area, measured by isothermal adsorption of argon at 77 K, of 76.9 m^2. The Grafoil was perforated with 0.5-mm-diam holes, spaced 5 mm apart in a regular array to facilitate mass flow. A Straty-Adams-type[12] capacitive strain gauge attached to the cell, was used to measure the pressure, giving a resolution of 10^{-4} atm in the vicinity of the melting curve. For convenience, all measurements were done below 318 mK, the minimum of the ^{3}He melting curve, since this provided a constant volume by means of the natural plug of solid ^{3}He in the 0.1-mm i.d. filling capillary. A cerium magnesium nitrate thermometer[13] was attached to the bottom of the cell allowing thermal contact to the ^{3}He through the copper body. The CMN thermometer was calibrated against the bulk melting curve of ^{3}He. Starting with a sufficient liquid density in the cell at high temperature, we maintained bulk solid in equilibrium with liquid over our entire calibration range.

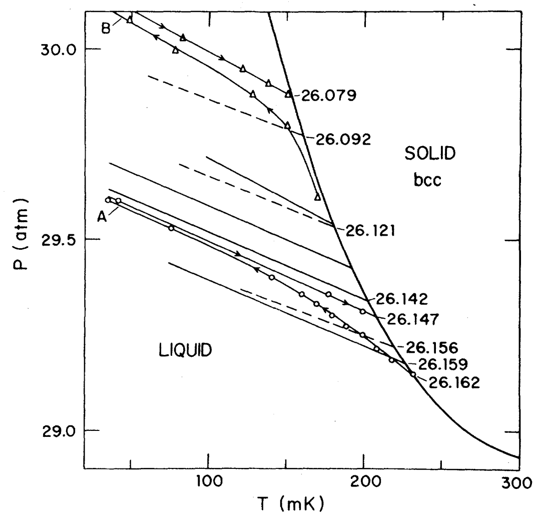

FIG. 1. Isopycnals for six of the densities studied are shown as solid lines which represent the equilibrium data points to an accuracy better than 10^{-2} atm. The isopycnals A (^{4}He precoating) and B (argon precoating) correspond to the melting of surface solid ^{3}He. The dashed lines represent isochores of the bulk liquid as calculated from previous measurements (Refs. 15 and 16). The five digit numbers indicate the liquid molar volumes (cubic centimeters/mole) measured by Trickey, Kirk, and Adams (Ref. 14).

The experiment itself consists of measuring the pressure of the bulk ^{3}He $P(z=\infty)$ as a function of temperature from 30 to 300 mK. We found that there are two different types of isopycnals depending on the history of the ^{3}He sample in the cell. Type 1 (nucleation) was always observed if the experiment started with liquid ^{3}He at a pressure below that of the low-temperature melting curve. Type 2 (melting) was observed if the cell was initially filled entirely with high-density solid ^{3}He; the bulk solid was then melted by slow decompression at constant temperature to prepare the sample at the melting curve. No similar hysteresis effect had been seen in the L-S experiment.

Our experimental data are shown in the P-T plane in Fig. 1. For the sake of clarity we did not include all of our data points. The solid lines show our data for the type-1 measurements where each label is the liquid molar volume determined at the melting curve by Trickey, Kirk, and Adams.[14] The bulk isoshores, shown as dashed lines calculated from previous measurements of thermal expansion[15] and compressibility,[16] differ somewhat from our type-1 data. We assume that possible uncertainty in the thermal expansion data are the reason for the discrepancy.[17] The type-1 data bear no resemblance to the L-S isopycnals. The contrast becomes apparent if we examine curves A and B in Fig. 1 that were observed after following the type-2 sample preparation. By measuring in a cooling direction from the bulk melting curve, we now observe a surface-solid isopycnal analogous to the L-S data. By cooling to a low enough temperature, so that $P(z=\infty)$ was at least 1 atm below the bulk melting curve, all accessible surface solid apparently melted. That is, upon any subsequent warming or cooling at this density, only the straight-line type-1 behavior can be seen.

In addition to the clear qualitative difference between the steady-state isopycnals observed in the type-2 measurement as compared with type 1, we observed a striking difference in the dynamic response of the system. After regulating the copper cell to a new temperature, held constant to ± 0.1 mK, the pressure along a type-1 isopycnal reached equilibrium with a time constant of approximately 0.1 h. Following the same procedure for the type-2 isopycnal, the pressure equilibrated much more slowly, with a time constant approaching 4 h close to the bulk melting curve. We suggest that this long time constant is due to the slow rearrangement of the surface solid layer, impeded by heat currents in the pores due to the large latent heat of melting.

The type-1 result is particularly surprising if one considers how large the local pressure must be at the interface between the existing triangular-symmetry adsorbed solid ^{3}He layer and the liquid. If we assume that the adsorbed layer extends out to $z=6$ Å, then Eq. (1) shows that $P(z)-P(z=\infty)=20$ atm. Thus even when $P(z=\infty)$ is very close to the bulk bcc solidification pressure, 20 atm of superpressurization of the liquid closest to the graphite is insufficient to nucleate the cubic lattice.

In the experiment of Bukshpan *et al.*[10] we thought that a residual layer of ^{4}He might have acted as a "matching" medium for nucleating surface-solid ^{3}He. To test this hypothesis we first added an amount of ^{4}He corresponding to one and then two adsorbed layers on our present Grafoil surface (curves labeled 26.121 and A, respectively, in Fig. 1). We found that this in no way alters the absence of nucleation described above, for pure ^{3}He. In addition, one layer of argon was also adsorbed on the recleaned Grafoil surfaces (curves 26.159 and B in Fig. 1). Crary and Vilches[18] had demonstrated recently that the argon substantially modified the nature of the first adsorbed He layer. However, in this case, too, no surface solidification of ^{3}He could be nucleated from the bulk liquid.

The absence of uniform nucleation should not be misconstrued as a demonstration that surface solid ^{3}He cannot exist in proximity with Grafoil. The type-2 experiment described above apparently introduced bulk solid into the pores of Grafoil as a result of solid growth from isolated nucleation sites. Such sites apparently do not occur on the surface of Grafoil. However, once solid does approach the Grafoil substrate the subsequent melting seems to be controlled by the van der Waals–field–induced local pressure. There appears to be a situation of metastability. It is not obvious to us which is the state of lower free energy.

Referring to curve A in Fig. 1, we can test whether the theory described by L-S is applicable. z_s, the thickness of the solid layer is calculated as in Ref. 1. Reasonable agreement with the simple theory is obtained by assuming that the fraction of the total area of the substrate covered with multilayered surface solid, a constant less than one, can be taken as an adjustable parameter, estimated to be $\frac{1}{2}$. In fact, curve A was measured after two layers of ^{4}He were adsorbed on the surface, confirming that as far as the influence of the van der Waals forces are concerned there is no difference between ^{3}He and ^{4}He. This is shown by the circles in Fig. 2. However, when the system was prepared by first preplating the Grafoil with one layer of argon, the theory of Ref. 1 no longer appears to be valid. This is shown by the triangles in Fig. 2 which were obtained by analyzing curve B of Fig. 1. The explanation might be that the layer of argon modifies the interaction between the substrate and the ^{3}He, producing a different functional form for the variation of the local pressure with the distance from the substrate.

In concluding we must stress that this type of experiment does not directly yield any microscopic details about the nature of the surface solid. Such information should be obtainable from

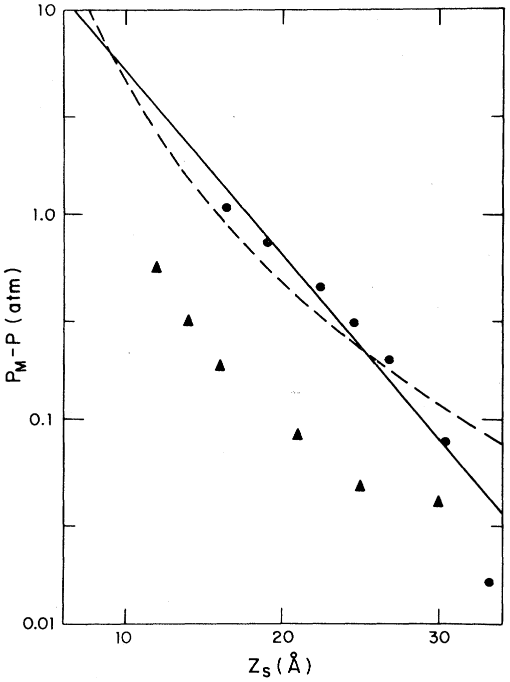

FIG. 2. The distance from the substrate to the liquid-solid interface z_S is shown for isopycnals A (circles) and B (triangles). P_M is the bulk melting pressure appropriate to the temperature where the bulk pressure P was measured. The solid line represents the ^{4}He data points presented in Ref. 1. The broken curve was determined by the theory of Ref. 1 using $\alpha = 2\times10^{-37}$ erg cm^3 as the van der Waals coefficient.

neutron scattering studies which have already told us that the first adsorbed layers of both ^{3}He and ^{4}He on Grafoil are close packed with a triangular symmetry.[4,7] In the case of ^{4}He this apparently leads to epitaxial growth of the bulk hcp solid phase. Actually the same situation may prevail for ^{3}He, where the hcp solid phase exists at much higher pressures, in the range of 100 atm. At low temperatures the lower-pressure bcc phase intervenes so that bulk hcp solid ^{3}He does not coexist with the liquid phase. This observation seems consistent with evidence, obtained recently by Bozler *et al.*[19] from NMR studies of surface induced ferromagnetism at millikelvin temperatures for pressurized liquid ^{3}He in Grafoil, that the surface solid layer varies in thickness between 0.86 layers at $P = 0$ to 1.19 layers at $P = 25.7$ atm. From a purely phenomenological viewpoint, we have shown that the adsorbtive solidification of ^{3}He on Grafoil from the bulk liquid phase belongs to the Class-II category of Dash[2] and Peierls.[3]

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

[2] J. G. Dash, Phys. Rev. B 15, 3136 (1977).

[3] Rudolph Peierls, Phys. Rev. B 18, 2013 (1978).

[4] M. Nielson, J. P. McTague, and W. Ellenson, J. Phys. (Paris), Colloq. 38, C4-10 (1977).

[5] K. Carneiro, J. Phys. (Paris), Colloq. 38, C4-1 (1977).

[6] H. Taub, L. Passell, J. K. Kjems, K. Carneiro, J. P. McTague, and J. G. Dash, Phys. Rev. Lett. 34, 654 (1975).

[7] K. Carneiro, W. D. Ellenson, L. Passell, J. P. McTague, and H. Taub, Phys. Rev. Lett. 37, 1695 (1976).

[8] Isopycnals are lines in a P, T diagram defined by a constant-volume system containing a constant number of atoms. On a microscopic scale, however, the density of the helium varies as a function of z, the distance from the substrate. See Ref. 1 for a detailed discussion.

[9] M. Cederbaum and J. Landau, Phys. Lett. 55A, 265 (1975).

[10] I. Bukshpan, M. Cederbaum, Y. Eckstein, J. Landau, and H. Levenwirth, in *Liquid and Solid Helium,* edited by C. G. Kuper, S. G. Lipson, and M. Revzen (Wiley, New York, 1975).

[11] D. F. Brewer, H. Mitchell, and W. S. Truscott, in Proceedings of the Symposium on Physics of Ultralow Temperatures, edited by T. Sugawara (to be published).

[12] G. C. Straty and E. D. Adams, Rev. Sci. Instrum. 40, 1393 (1969).

[13] Cerium magnesium nitrate (CMN) self-contained thermometer package was generously provided by Dr. B. M. Abraham, Argonne National Laboratory.

[14] S. B. Trickey, W. P. Kirk, and E. D. Adams, Rev. Mod. Phys. 44, 668 (1972).

[15] A. C. Anderson, W. Reese, and J. C. Wheatley, Phys. Rev. 130, 495 (1963).

[16] E. R. Grilly, J. Low Temp. Phys. 4, 615 (1971).

[17] A less plausible possibility is that the regions of liquid at densities larger than bulk, due to the high local pressures, are responsible for the discrepancy. This problem has been considered for liquid ^{4}He by H. Wiechert and G. Wupperfeld, J. Phys. (Paris), Colloq. 39, C6-324 (1978).

[18] S. B. Crary and O. E. Vilches, Phys. Rev. Lett. 38, 973 (1977).

[19] H. M. Bozler, T. Bartolac, K. Lucy, and A. L. Thomson, J. Phys. (Paris), Colloq. 39, C6-283 (1978).