Role of Substrate Symmetry in Nucleating Solid Helium

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The continuous nucleation of bcc solid ^{3}He from the liquid phase due to the presence of a MgO substrate is detected. For superfluid ^{4}He there is no evidence of continuous nucleation of either the hcp or the bcc solid from the substrate. The experiment contrasts the influence of the square lattice of MgO with the triangular lattice of a basal-plane graphite substrate. The phenomenon of pore condensation for solid ^{3}He is discussed.

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In this paper we present new results which compare the onset of solidification of ^{3}He and ^{4}He on a magnesium oxide substrate, which has cubic symmetry, with that already reported[1,2] for solidification on Grafoil, which has a hexagonal symmetry. The Grafoil experiments had shown that hcp ^{4}He undergoes continuous solid nucleation whereas, surprisingly, bcc ^{3}He did not nucleate similarly. Since the van der Waals forces between the substrate and either isotope are identical, and this force is considered[1] to be responsible for the superpressurization of the first few helium layers on the substrate, we were led to suggest that the substrate symmetry (hexagonal graphite encouraging the hcp ^{4}He) is the determining factor in the onset of solidification. To test this conclusion we repeated the experiments with a MgO substrate[3,4] which has a cubic symmetry. For this substrate we observed uniform nucleation of the bcc ^{3}He whereas ^{4}He does not show any signs of surface solidification in either hcp or bcc regions.

We should emphasize that the experiment on Grafoil alone did not prove the relevance of substrate symmetry. During the condensation of the first layer of He on Grafoil, it is known from adsorption studies[5] that initially an ordered state is reached in which the helium atoms are registered with the graphite lattice. Subsequently, as the coverage is increased, a close-packed triangular two-dimensional lattice is formed, with a spacing incommensurate with the graphite lattice. It can then be argued that this layer, which is formed by either isotope, is the natural base for the continuing growth of hcp ^{4}He, whereas it would not encourage the further growth of a bcc solid. The present experiments disprove the universality of this model, and demonstrate the importance of a matching substrate symmetry. Further experimental evidence from direct observation of the growth of aligned ^{4}He crystals on the Grafoil substrate will also be presented to support the conclusion.

The experimental evidence for the onset of solidification is deduced from the measurement of equilibrium points along isopycnals[6] in the vicinity of the bulk melting curve. There appears a substantial difference between the isopycnal and the isochore for the bulk liquid when surface solidification occurs, in the presence of a substrate of sufficiently large surface area. The present experiments used a 2.9-g MgO sample prepared from compressed smoke at the University of Washington.[3] Its properties have been measured by Dash *et al.*[4] who showed that it produces krypton steplike adsorption isotherms and that it consists of cubes of 0.1-μm–average-size exposed faces having square symmetry. This allows us to estimate that our sample had an exposed surface area of about 20 m^2, and an open volume of 4.3 cm^3 for the helium sample.

Experiments were performed in a 6.3-cm^3 copper cell connected to a Straty-Adams type[7] pressure transducer, into which the MgO sample was transferred from an evacuated quartz ampule. To promote thermal equilibrium, the interior of the cell was crisscrossed by several copper wires. During the ^{3}He experiments we observed the existence of two distinct regions in the P, T plane distinguished by widely differing thermal time constants τ. The approach to thermal equilibrium was monitored by measuring the pressure in the cell (the transducer allowed a resolution of better than 10^{-4} atm) while the thick copper walls were maintained at constant temperature by the dilution refrigerator. Far from the bulk melting curve we observed $\tau \simeq 0.5$ h. When the pressure was within 0.1 atm of the melting curve we observed a much slower approach to equilibrium, $\tau \simeq 4$ h. During the ^{4}He experiments the presence of the superfluid decreased the time constant to $\tau \leqslant 30$ sec. For ^{3}He, we established a constant-volume system by allowing a block of solid ^{3}He to form in the filling tube; for ^{4}He samples, we actuated a needle valve

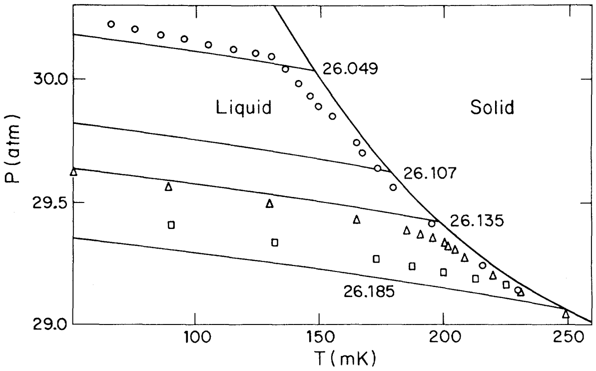

FIG. 1. Isopycnals for ^{3}He on MgO substrates are shown by the circles, triangles, and squares. Data taken while moving toward the melting curve over a period of approximately two days. The solid lines, corresponding to bulk liquid isochores reported in Ref. 2, are identified by their molar volumes (cm^3/mole). The melting curve is from Ref. 8.

at the base of the ^{4}He bath space. A cerium-magnesium-nitrate magnetic thermometer was attached to the bottom of the cell.

Figure 1 shows isopycnals in the vicinity of the bulk melting curve measured for ^{3}He on MgO compared with previous results for bulk isochores, and Fig. 2 for ^{4}He. The new results on the MgO substrate show, for ^{3}He, a substantial difference between the isopycnal and the isochore. In contrast, the results for ^{4}He, in both the hcp and the bcc regions, show that there is no difference between the two, even to the extent that supercooling can be observed (Fig. 2 inset). The results indicate that ^{4}He neither solidifies continuously over the MgO surface nor even forms isolated nucleation centers which would prevent supercooling.

Since these experiments were devoted to studying the nucleation of solid helium, all isopycnals shown in Figs. 1 and 2 were measured starting in the bulk liquid phase far from the melting curve. In the case of ^{3}He this meant that small quantities of heat were applied to the copper wall of the cell to proceed to progressively warmer equilibrium points. Thus during the approach to equilibrium the ^{3}He-Cu interface was slightly hotter than the ^{3}He-MgO interface. If all surface properties were equal this would imply a greater likelihood for solid ^{3}He to nucleate on the Cu. The large displacement of the isopycnal from the isochore as well as the large increase in the thermal time constant demonstrates that surface solid ^{3}He coats the MgO substrate.

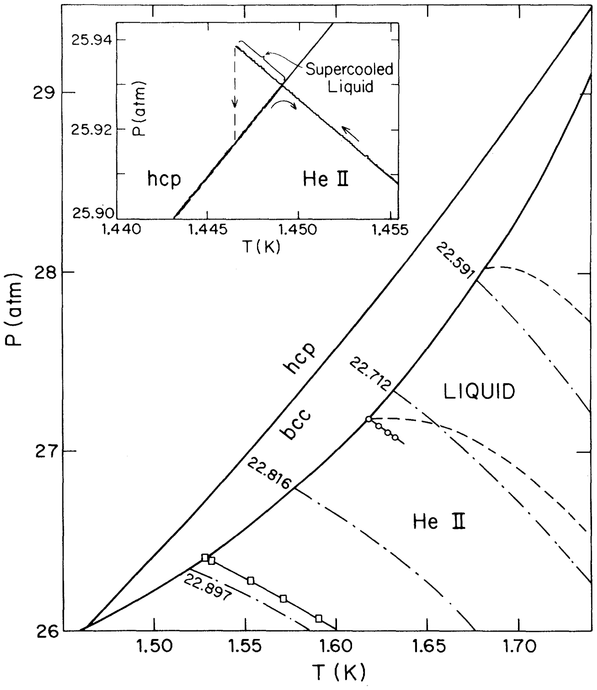

FIG. 2. Isopycnals for ^{4}He on MgO substrates (circles and squares) compared to ^{4}He on Grafoil substrates, dashed curves (Ref. 1). The broken curves, identified by their molar volumes (cm^3/mole), are bulk liquid isochores (Ref. 1). An enlarged isopycnal for MgO is shown in the inset, corresponding to a slow continuous trace.

The exact form of the displacement of the melting curve for the ^{3}He on MgO from the bulk result[8] can be understood approximately; it shows evidence for the initial formation of several uniform atomic layers of solid, followed by condensation in the pores between the cubic MgO crystallites. The initial stage is identical to that analyzed by Landau and Saam,[1] and we show in Fig. 3 (broken curve) the calculated thickness Z_s of the solid layer[1] as a function of the deviation from the bulk melting curve $P_M(T) - P(T)$, for an assumed MgO-^{3}He interaction constant $\beta = 1.7 \times 10^{-37}$ (cgs). This curve agrees with the experimental results only to a thickness of about 30 Å. The pore condensation then starts to be felt. It can be treated in a manner analogous to that of Bienfait, Dash, and Stoltenberg[9] who discussed the case of ^{4}He adsorbed from the vapor phase. The existence of surface tension in the pores results in an atomically rough[10] solid surface being concave. Therefore, the solid is at higher pressure than the liquid in equilibrium with it. The interface between solid and liquid is the surface on which

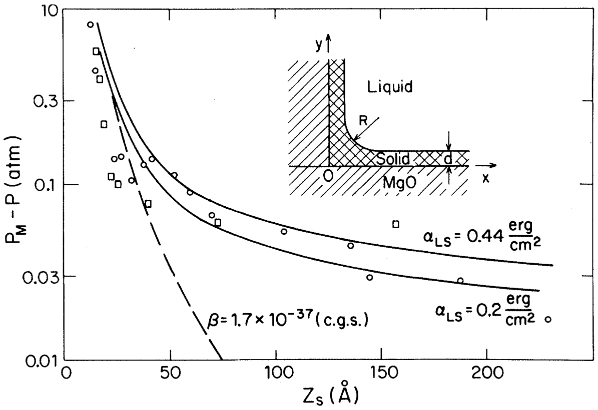

FIG. 3. The calculated ^{3}He surface solid layer thickness as a function of $P_M - P$. The circles and squares are from Fig. 1. The solid curves are from Eq. (3), and the dashed curve is from Ref. 2. The inset is discussed in the text.

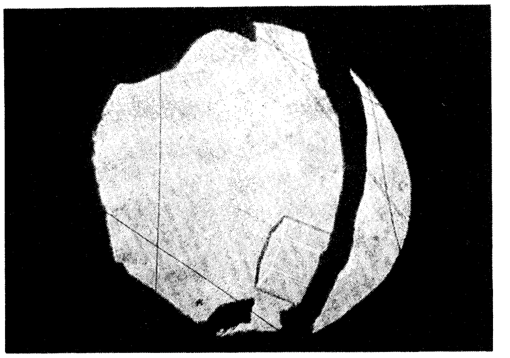

FIG. 4. Photograph of a single hcp ^{4}He crystal that nucleated on a Grafoil substrate with its basal plane parallel to the basal plane of the Grafoil. The Grafoil strip, appearing as an uneven black band in the picture, has its basal plane surfaces oriented nearly perpendicular to the optical windows.

the sum of applied pressure $P(T)$, the substrate attraction, and the surface tension pressure difference is equal to the bulk melting pressure $P_M(T)$:

$$P_M = P + \beta(x^{-3} + y^{-3}) + 2\alpha_{LS}/R(x, y). \quad (1)$$

The coordinate system is shown in Fig. 3 (inset) and α_{LS} is the liquid-solid surface tension.[11] An approximate solution of (1) is obtained by first considering the layer remote from an including corner, where the radius of curvature $R \to \infty$. There, $P_M - P = \beta/d^3$. Close to a corner we assume that the pore condensation effect is dominant, and that the surface has the form of a cylinder of radius $R = \alpha_{LS}/(P_M - P)$. When the length of each reentrant edge is l, the total volume of condensed solid in one corner is therefore

$$2l^2 d + R^2 l(1 - \pi/4). \quad (2)$$

Dividing by the total surface area of the corner, $2l^2$, gives a mean solid thickness Z_s which is written in terms of the melting pressure displacement $(P_M - P)$ as

$$Z_s = \left(\frac{(P_M - P)}{\beta}\right)^{-1/3} + \frac{(1 - \pi/4)\alpha_{LS}^2}{2l}(P_M - P)^{-2}. \quad (3)$$

In Fig. 3 this result is also plotted (full line) and shows reasonable agreement with the data when $l = 1000$ Å (from Ref. 4) and $\alpha_{LS} = 0.44$ erg cm^{-2}. The latter value for ^{3}He can be compared with $\alpha_{LS} = 0.084$ erg cm^{-2} for bcc ^{4}He measured by Landau *et al.*[11] However, it is obvious that confirmation of the pore condensation model comes from the $(P_M - P)^{-2}$ dependence of the second term in (3); the exact value of the coefficient $(1 - \pi/4)\alpha_{LS}^2/2l$ is dependent on geometrical parameters[12] such as l, the angle between the faces, and the distribution of pore sizes.

There remains the question of why bcc ^{4}He is similar to hcp in its refusal to nucleate on MgO in light of our demonstration of the importance of substrate symmetry. The pertinent fact is the very restricted region of existence of the bcc ^{4}He phase. Even if the surface layer [at $P_M(T)$] happens to be in the region where bcc is stable, the layers beneath it are at substantially higher pressures, where the hcp is stable, and so the nonmatching argument still applies. The hypothesis is strengthened by the recent neutron scattering results of Wiechert, Lauter, and Stühn.[13] They showed, for ^{4}He on Grafoil at pressures $P < P_M$, that the [100] hcp Bragg peak could be detected even at temperatures where bcc is the stable phase at $P_M(T)$. These ideas can be tested when neutron scattering experiments are performed for ^{3}He and ^{4}He adsorbed on MgO.

Further evidence of the importance of the right substrate symmetry for the nucleation of ^{4}He is seen in the form of macroscopic crystals grown on Grafoil substrates. Balibar, Castaing, and Laroche[14] have found, by using heat-pulse propagation techniques to deduce the orientation, that ^{4}He crystals grow with their c axis consistently normal to the exposed graphite basal plane when the Grafoil sample had been preheated to desorb all impurities. When Balibar, Castaing, and Laroche[14] allowed air to contaminate the Grafoil surface it was no longer possible to obtain oriented crystals. Using an optical cryostat we have confirmed this, by observing the orientation of ^{4}He crystals nucleated on clean Grafoil (Fig. 4). For other materials, both Landau *et al.*[11] and Balibar, Castaing, and Laroche[14] found that single hcp crystals do not generally wet copper or glass as well as the superfluid ^{4}He does (contact angle > 90°). It will be very interesting if clean single crystals of MgO nucleate oriented bcc ^{3}He crystals.

In conclusion, we should reemphasize the analogy to the adsorption results from the vapor phase. As in the case of hcp ^{4}He on Grafoil we now find that bcc ^{3}He on MgO belongs to the class I category of Dash[15] and Peierls.[16]

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Distance-Dependent Relaxation Shifts of Photoemission and Auger Energies for Xe on Pd(001)

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Photoelectrons and Auger electrons from Xe in adsorbed multilayers of Xe on Pd(001) as well as on spacer layers of Kr on Pd(001) exhibit well-resolved increases in kinetic energy with decreasing distance from the surface (2–28 Å), allowing a direct labeling of the layers. These relaxation shifts for core-hole excitations (0.9–2.1 eV) and for Auger excitations (3.3–6.6 eV) are well described by an image potential, where the position of the image plane agrees within 0.2 Å with local-density functional theory.

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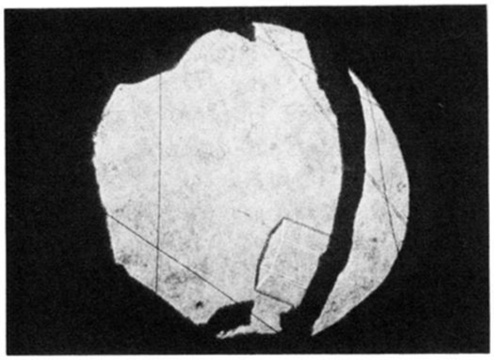
Core-level binding energies and Auger electron energies for adsorbates are shifted relative to their free-atom counterparts by initial-state potential-energy effects and by hole-relaxation (polarization) effects. For physisorbed species on metals, relaxation effects due to the screening of excited hole states by the metal surface are of central importance. Extensive theoretical work on single-hole and two-hole relaxation effects has been reported[1-5] but no clear-cut experimental tests have been performed, in part because of the difficulty of separating initial-state and final-state effects. In this respect, rare-gas atoms are especially attractive in that initial-state chemical effects are expected to be minimal. To date, however, rare-gas core-level binding energy shifts have only been studied for atoms implanted in metals[6] and semiconductors,[7] for which initial-



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