Novel Wetting Behavior of ^{4}He on Cesium

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We have measured ^{4}He adsorption isotherms on a cesium substrate above and below T_λ using a quartz microbalance technique. The results show that the cesium surface remains dry until the pressure almost reaches the saturated vapor pressure. At liquid-vapor coexistence, however, the wetting film continuously thickens to more than 30 layers. Below T_λ the film at coexistence is superfluid. Above T_λ we resolve a feature in the isotherm just below saturated vapor pressure which is characteristic of a prewetting transition.

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Liquid helium and particularly superfluid helium are found to form thick films on all conventional substrates. This experimental fact is theoretically substantiated by observing that the helium-helium interaction is extremely weak, and the energetic cost of forming an additional interface at the solid-liquid boundary is more than compensated for by taking advantage of the attractive $1/z^3$ van der Waals field of the substrate. In a recent paper [1], Cheng, Cole, Saam, and Treiner (CCST) showed that this energetic balance is qualitatively different for the case of helium adsorbed on alkali-metal substrates. Although the long-range $1/z^3$ field of these substrates is only slightly weaker than conventional materials such as graphite or gold, the short-range part of the potential is much weaker because the electrons in the alkali metals extend quite far from the surface, and the electron-electron repulsion forces the adsorbed atoms to maintain a large equilibrium distance. This effect causes helium to be less tightly bound to the surface of cesium and rubidium than to bulk liquid helium [2]. CCST predict two different types of behavior for adsorption on alkali-metal substrates depending on the details of the potential: nonwetting, in which the substrate remains dry even at liquid-vapor coexistence, and prewetting, in which thin films at $T=0$ K are unstable, but films thicker than a certain critical thickness can form on the substrate. For the helium-cesium adsorption potential, CCST predict nonwetting. This prediction has been experimentally supported by recent results [3] of Nacher and Dupont-Roc (ND) in which superfluid film flow was interrupted by a cesium barrier.

The experimental technique used by ND is restricted to the case of liquid-vapor coexistence, and is sensitive only to the superfluid fraction of the film. Because it relies on superfluidity, their technique cannot be used to study adsorption above the lambda point. In this paper, we present experimental results on the adsorption of helium on cesium using a complementary technique, the quartz microbalance, which is sensitive to the nonsuperfluid part of the adsorbed film. In the quartz microbalance technique, the shifts in the resonant frequency of a crystal can be related to the mass of the viscously clamped adsorbed film. The superfluid transition can be observed as an apparent drop in mass, since the superfluid fraction of the film has zero viscosity. This technique has been used in several previous studies of helium adsorption on conventional substrates [4-6]. Since the microbalance directly detects the normal fluid, the experiments can be done at temperatures above and below the lambda point, and can also be conveniently done as a function of gas pressure from zero to the saturated vapor pressure.

Cesium is one of the most reactive elements (it burns spontaneously in air) and the adsorption potential is very sensitive to surface contamination, so forming and maintaining a clean substrate was a primary goal in the design of our apparatus. Our cesium substrates were formed by evaporation in an ultrahigh-vacuum environment provided by the 4-K walls of the apparatus and special care was taken to avoid impurities in the helium gas used for the isotherms, since even parts per 10^6 concentrations of oxygen would contaminate the cesium.

In this paper, we present adsorption isotherms on cesium and, for comparison, on a gold substrate. The gold electrodes deposited on the crystal by the manufacturer served as the substrates for the gold isotherms. After the gold isotherms were completed, the cesium substrates were evaporated onto the gold electrodes of the same crystal.

The apparatus consisted of a 5-MHz *AT*-cut quartz crystal microbalance and a cesium evaporator mounted inside a vacuum can immersed in liquid ^{4}He. The crystal was mounted in a vertical plane approximately 2 cm from the cesium evaporator on a holder that could be rotated to deposit cesium on both sides of the crystal. Evaporation masks that allowed the gold electrodes to be covered with cesium were mounted on the holder within 0.1 cm of the crystal. The mass sensitivity of a quartz microbalance is strongly localized over the electrodes [7]. The cesium evaporator consisted of a resistively heated stainless-steel enclosure. It was plated with gold and mounted on nylon stand-offs to minimize its thermal coupling to the rest of the apparatus. Only the neck of the argon-gas-filled glass ampule in which the cesium was supplied protruded from the evaporator. The evaporator was surrounded by copper walls thermally anchored to large copper rods in contact with the liquid-^{4}He bath.

The copper wall between the crystal and the evaporator was a movable shutter used to start and stop the cesium deposition on the crystal and to break the neck of the cesium ampule. The ^{4}He gas used in the adsorption experiment was admitted to the vacuum can through a 5-m-long copper capillary tube and a low-temperature throttle valve that were both located in the helium bath. This ensured that all impurities in the gas were frozen out.

The apparatus was evacuated to a pressure of 4×10^{-6} Torr at room temperature and then the walls of the vacuum can were cooled to 77 K. For the cesium isotherms the cesium ampule was broken at this point and the apparatus reevacuated to 4×10^{-6} Torr. Next, the apparatus was immersed in liquid ^{4}He boiling at 4.2 K. Since the thermal time constant of the quartz crystal in high vacuum was about 1 h, the temperature of the crystal remained high while the walls of the vacuum can quickly reached 4.2 K. This pumped volatile impurities from the microbalance and onto the walls of the can. For a cesium study the evaporator was heated (with a total power of approximately 3 W) and outgassed just after the immersion in the helium bath. During the outgassing, the shutter was closed and the crystal was completely isolated from the evaporator. The vigorously evaporating cesium could getter any outgassed impurities. Then the shutter was opened exposing the crystal to the 0.63-cm-diam aperture of the evaporator, and 300 nm of cesium deposited on each side of the crystal. During the evaporation every surface surrounding the crystal, except for the evaporator aperture, was at or below 7 K while the crystal itself was at approximately 150 K. Extrapolation of the vapor pressure of solid oxygen indicates that the time required for the formation of a monolayer of oxygen at 7 K is essentially infinite. Finally the entire apparatus was allowed to stabilize at a low temperature for the measurement. To generate an isotherm small doses of cold ^{4}He gas were admitted to the vacuum can. After each dose the pressure was measured with a room-temperature capacitive pressure gauge and the resonance line shape was measured by a technique based on that of Lea, Fozooni, and Retz [8]. The mass sensitivity was approximately 5 layers/Hz of frequency shift. The measuring circuit dissipated less than 1 nW in the crystal. The thickness resolution is about 0.1 statistical layer of ^{4}He and the temperature stability is about 1 mK.

Figure 1 shows two adsorption isotherms measured at 2.7 K. All of the isotherms shown here have been corrected for viscous loading by the gas [6] and for the pressure dependence [8] of the resonant frequency of the crystal. The gold isotherm shows conventional adsorption behavior. As the pressure increases, the adsorbed mass gradually grows. As the bulk liquid-vapor pressure P_0 is approached, the mass rapidly increases until the films are tens of layers thick. The film on gold grows monotonically and smoothly. The behavior of the adsorbed film on cesium is strikingly different. To within 0.2 Hz the frequency does not shift until the pressure reaches 130 Torr, within 5% of P_0, which means that less than a monolayer or so adsorbs in this pressure range [9]. In this pressure range, the adsorbed film is much thinner on cesium than on gold. Very near P_0, a small foot abruptly develops in the cesium isotherm before the thickness smoothly diverges at P_0. This region of the isotherm is shown in more detail in Fig. 2. Not shown in the figures is the

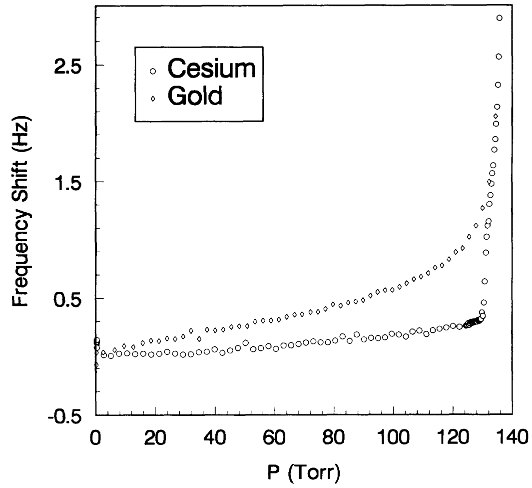

FIG. 1. Adsorption isotherms of ^{4}He on cesium and gold substrates at 2.7 K. The thickness sensitivity is 5 layers/Hz. Below 130 Torr the cesium film thickens less rapidly than the gold film. Above 130 Torr the cesium isotherm shows a foot before growing to maximum depth whereas the gold isotherm is smooth. The foot is shown in an expanded scale in Fig. 2. Not shown is the maximum frequency shift at coexistence, about 6 Hz, corresponding to 30 layers, for both films.

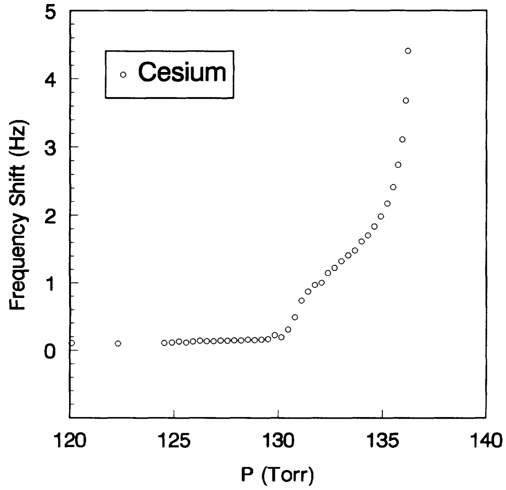

FIG. 2. The region near P_0 on the 2.7-K cesium isotherm of Fig. 1. The sharp increase in frequency shift near 131 Torr marks the surface phase coexistence region of a prewetting transition.

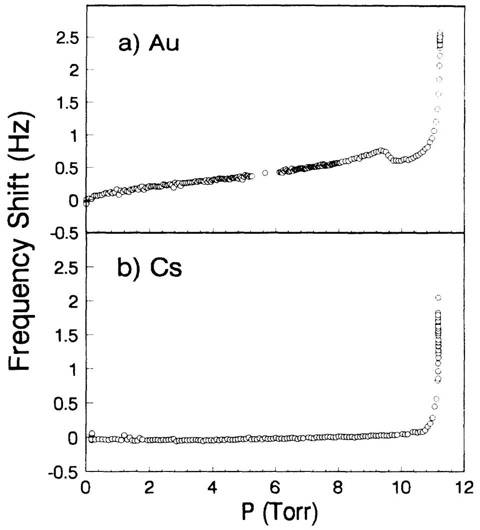

FIG. 3. Isotherms at 1.75 K. (a) A gold isotherm. The frequency shift increases monotonically until a cusp develops at about 9 Torr. As discussed in Ref. [4] this cusp signals superfluid onset. (b) A cesium isotherm. The frequency shift remains small until just below saturated vapor pressure and then thickens rapidly. The near equality of the maximum frequency shifts, 2.5 and 2.0 Hz for gold and cesium, respectively, indicates nearly equal normal masses at saturation.

maximum frequency shift at P_0. The maximum frequency shift is 5.6 Hz for the gold isotherm and 6.6 Hz for the cesium isotherm. Both films thicken to about thirty layers [10].

Analogous isotherms measured below T_λ at 1.75 K are shown in Fig. 3. Figure 3(a) shows an isotherm on gold. The cusp near 9 Torr is due to superfluid onset. Isotherms like these were first measured and interpreted by Chester, Yang, and Stephens [4]. After superfluid onset, the frequency shift is determined only by the normal component of the film, which decreases faster with pressure than the total thickness increases; this effect causes the downward-going part of the cusp. Finally the amount of normal fluid grows rapidly as the saturated vapor pressure is approached and the total thickness diverges. Figure 3(b) shows an isotherm on cesium. The frequency shift is zero until just below the saturated vapor pressure. Then there is a small upturn at the limit of our frequency resolution just below saturated vapor pressure. At P_0 the frequency shift increases until the total shift is nearly the same as it is for the isotherm on gold in Fig. 3(a). This shift is approximately one-third of the shift observed at saturation in the 2.7-K isotherms, which is consistent with the expected superfluid fraction at 1.75 K. A feature like the foot in Fig. 2 is either absent or unresolved on the 1.75-K isotherm.

These data show that the adsorption of helium on cesium is distinctly different than on conventional substrates. For vapor pressures from 0 to approximately $0.95P_0$, a cesium surface adsorbs less than one layer of solid or normal liquid helium. Near P_0, however, the film continuously thickens. Both above and below T_λ, the frequency shift at coexistence is not appreciably different from the frequency shift on a gold substrate. Above the lambda point, this implies that the film thicknesses are the same. Below the lambda point, this implies only that the mass of normal fluid is the same, but there is no reason to suppose that the superfluid fraction in such thick films is not the same on both substrates. In contrast to gold, however, the onset of superfluidity on cesium appears to occur extremely close to P_0. These results show that, in the technical sense, helium wets cesium.

Our results are in apparent conflict with those of ND, since their experiment was done at $P=P_0$ where our data show the formation of a thick film. Comparison with the results on gold suggests that the film is superfluid. Because the substrates were prepared in different manners under very different conditions, differences in the structure or chemical contamination of the cesium surfaces may account for the differences in the wetting behavior. The resolution of this point must await systematic surface characterization studies.

Our results are also in conflict with CCST's nonwetting prediction for cesium. However, the foot in Fig. 2 is characteristic of prewetting, which is predicted by CCST for other alkali metals with slightly stronger adsorption potentials than cesium. Prewetting is a first-order transition between two coexisting surface phases of different thickness which occurs at constant chemical potential. As additional atoms are added to the system at the coexistence chemical potential, the adsorbed mass continuously increases as the area covered by the thicker phase grows at the expense of the thinner one. The experimental signature of a prewetting transition in an isotherm is, therefore, a vertical but continuous step at constant pressure. Although the step shown in Fig. 2 is not vertical, it is possible that structural inhomogeneities could smear the transition. The difference in thickness Δd between the coexisting phases is approximately four layers at $T=2.7$ K. Prewetting has also been reported in a recent experiment investigating helium on hydrogen [11]. In both these cases the challenge is to reconcile the experimental results with substrate-adsorbate interaction potential strengths.

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[9] Because the corrections for the gas effects are relatively large at this high temperature, uncertainties in them may contribute to the frequency shift at the 0.1-Hz level. However, since the same corrections were made to the gold isotherm the difference between these curves is unaffected by these uncertainties.

[10] At the saturated vapor pressure, the chemical potential of the film is extremely close to the bulk chemical potential, and depends very weakly on the film thickness. The observed film thickness at saturation is a result of a balance between a number of small effects including gravity, substrate topography and surface tension, and residual temperature gradients at the microkelvin level.

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