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Adsorption of ^{3}He on Cesium

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Adsorption isotherms of ^{3}He on cesium substrates have been measured in the temperature range from 0.2 K to 1.5 K. At liquid-vapor coexistence ^{3}He wets cesium at all temperatures studied. Step-like features are found in the isotherms which are similar to the prewetting transitions of ^{4}He on Cs substrates, but the width of these steps is ~20 times wider for ^{3}He than for ^{4}He. In the case of ^{3}He on Cs, the steps are located at a chemical potential about 0.6 K below liquid-vapor coexistence. If the low temperature behavior is interpreted to be first order prewetting, the prewetting critical point temperature is 0.6 ± 0.1 K.

I. INTRODUCTION

The manner in which a liquid film grows on a surface as bulk coexistence is approached is determined by the binding strength of the surface. On a strongly binding substrate the attractive surface potential serves to stabilize the liquid phase so that wetting films grow smoothly and continuously as bulk coexistence is approached. In contrast, on a weakly binding substrate the free energy balance is more subtle, and the growth may proceed through a first order film thickness transition known as prewetting.[1,2] The locus of prewetting transitions in the $P-T$ (or $\mu-T$) plane is the prewetting line. The prewetting line typically intersects the bulk coexistence line at a first order wetting transition and extends upwards in temperature where it ends at a prewetting critical point. The first example of a prewetting phase diagram was found in studies of the adsorption of ^{4}He on cesium,[3] and the phenomena has subsequently been observed in a number of systems.[4–6]

Since the liquid-vapor surface tension of ^{3}He is much smaller than that of ^{4}He, ^{3}He is expected to wet cesium down to zero temperature.[7] Despite the fact that there is no wetting transition in the ^{3}He/Cs system, theoretical

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predictions indicate that wetting should occur via a prewetting transition.[7] In this case the prewetting line would not intersect the bulk coexistence line but would instead terminate at zero temperature at a chemical potential below coexistence. The theory of Ref. 7 also suggests that the Fermi statistics of the ^{3}He should play an important role in the prewetting behavior, and should result in a series of smaller film thickness transitions in addition to a prewetting transition.

Previous work in this laboratory[8] studied the adsorption of ^{3}He on Cs at 1.2 K. One of the conclusions of the previous study was that if prewetting occurs in this system, the prewetting critical point temperature lies well below 1 K. The purpose of the work reported here is to extend these measurements to as low a temperature as possible and to reexamine the question of prewetting. We were able to obtain adsorption isotherm measurements of ^{3}He on Cs down to 0.2 K. Below this temperature the equilibrium time for the experiment became prohibitively long. As expected ^{3}He wets cesium at all temperatures. Additionally, the ^{3}He films thicken at a broadened step in the isotherms located at a chemical potential about 0.6 K below saturation. As the temperature is lowered the steps become steeper until 0.6 K where the steepness of steps becomes constant. This general behavior of the steps is reminiscent of the ^{4}He prewetting line. However, the steps at their sharpest remain ~20 times wider for ^{3}He than for ^{4}He prewetting steps on the same substrates and by naive comparison do not look like first order transitions. In order to decide whether first order prewetting does occur in the ^{3}He/Cs system, one must reconcile these two apparently conflicting observations. Our attempts to do so are discussed below.

II. EXPERIMENT

We have measured adsorption isotherms using a quartz crystal microbalance.[9,10] The microbalances were used at their third harmonic at a frequency of ~5.5 MHz, so that their mass sensitivity was approximately 0.133 Hz/monolayer of liquid ^{3}He. The apparatus consisted of an OFHC copper vacuum can which contained two microbalances. Cesium was evaporated from a source of pure elemental metal onto both electrodes of one of the microbalances. The microbalance and the vacuum can were maintained at a temperature less than ~6 K during the evaporation to avoid contamination of the highly reactive cesium surface. The second microbalance was left with bare gold electrodes. The purity of the ^{3}He used was >99.999%.

Measurements were conducted on three different cesium substrates. The first was studied down to ~0.4 K using a recirculating ^{3}He refrigerator for cooling, while for the second and third surfaces the temperature range was extended by installing a dilution refrigerator. In order to concentrate on the steepness of the steps, most of the isotherms in the third set of data were not run completely to saturation. Consequently, the steepness of the steps was accurately measured but their location was not. The positions of the steps measured in the first two data sets and in the completed isotherms of the third data set are identical within the accuracy of the experiment. The measured steepness of the steps $(-df/d\mu)$ varied by ~30% from one surface to the next, though in each case the temperature dependence of the steepness was similar.

In order to assess the effect of substrate inhomogeneity on the prewetting behavior, the substrates were annealed. This was done by warming the cesium coated microbalance to approximately 80 K for about 30 minutes. During annealing, the vacuum can was again maintained at a temperature below ~6 K. Measurements were made on the first substrate both before and after annealing, while the second and third surfaces were annealed immediately after they were evaporated.

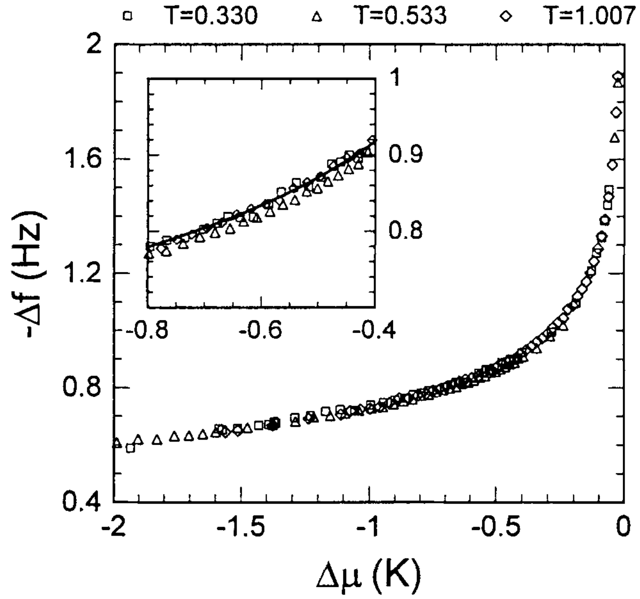

Fig. 1. Adsorption isotherms of ^{3}He on Au used for the chemical potential measurement at low temperatures, where the vapor pressure was too small to be measured with a manometer. The inset graph is a magnification of the plot about the region where the steps in the ^{3}He isotherms were found. The solid line through the data shows the fitted curve used for the measurement.

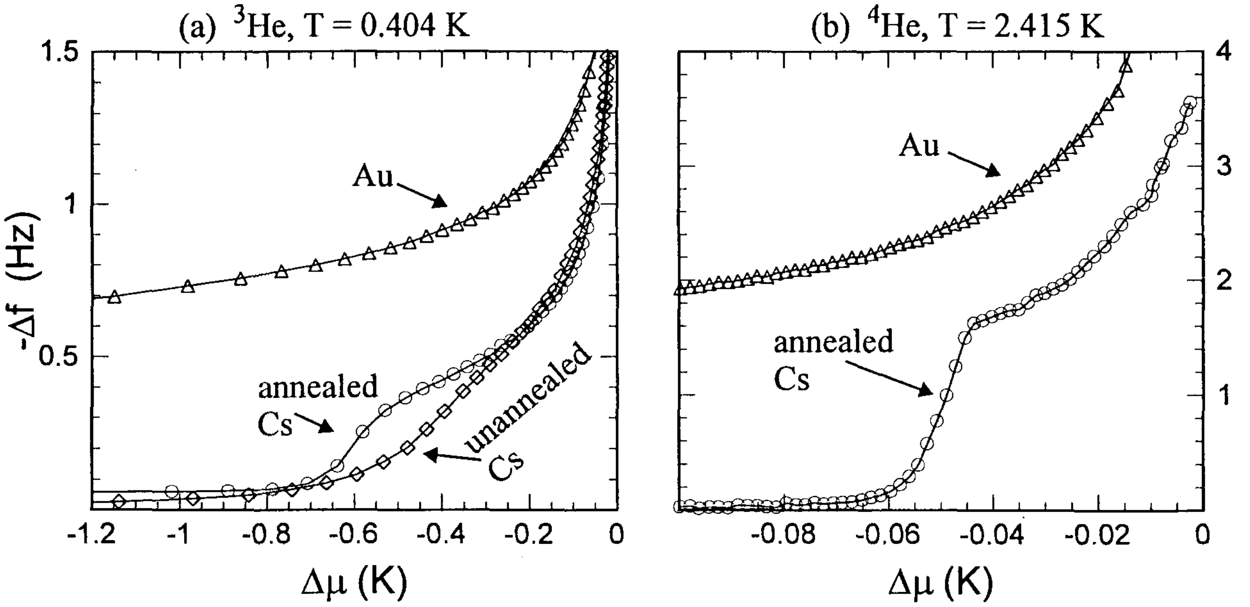

Fig. 2. Adsorption isotherms for ^{3}He and ^{4}He on gold and cesium. (a) ^{3}He on Au, annealed Cs, and unannealed Cs at $T = 0.404$ K. (b) ^{4}He on the same Au and annealed Cs substrates at $T = 2.415$ K.

The experimental results are presented as the shift of the resonant frequency of the microbalance, $-\Delta f$, as a function of the chemical potential of the ^{3}He as shown in Figs. 1–3. Because the saturated vapor pressure of ^{3}He spanned 6 orders of magnitude over the temperature range of this experiment, a variety of techniques were required to measure the chemical potential. For temperatures above ~0.55 K a room temperature capacitance manometer was used to determine the pressure. For temperatures between ~0.3 and ~0.6, an *in situ* capacitance manometer was used. In these two cases $\Delta\mu$ was calculated from the pressure using the usual ideal gas approximation, $\Delta\mu \equiv \mu - \mu_0 = T \cdot \ln(P/P_0)$. Here μ_0 and P_0 are the chemical potential and pressure at liquid-vapor coexistence, respectively.

Below ~0.3 K the pressure was too small to be accurately measured with the *in situ* manometer, so a new technique had to be devised to measure $\Delta\mu$. We found that the gold plated microbalance could be used as a chemical potential meter. This technique relies on the observation that the frequency shift of the gold plated microbalance is a function of only the chemical potential offset, independent of temperature.[11] This behavior can be seen in Fig. 1 which shows the frequency shift of the gold plated microbalance plotted vs. $\Delta\mu$ for three different temperatures, $T = 0.330$ K, $T = 0.533$ K, and $T = 1.007$ K. A fit of the isotherm at $T = 0.330$ K was used to convert the measured frequency shifts of the gold-plated microbalance to

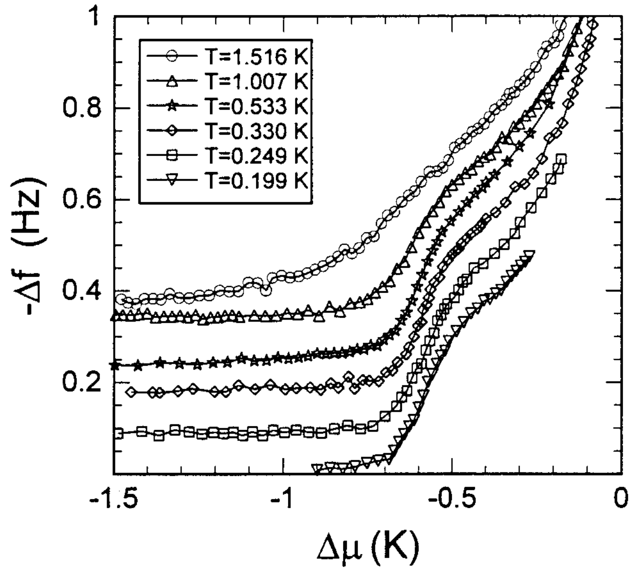

Fig. 3. Adsorption isotherms for ^{3}He on annealed Cs at temperatures ranging from ~0.2 K to ~1.5 K.

chemical potentials. The inset graph of Fig. 1 shows the data and the fit curve for chemical potential offsets near the location of the steps found in the ^{3}He adsorption isotherms. The ~10 mHz shift between the 0.533 K data and the other two data sets provides an estimate for the error in this measurement method, which in this case leads to a systematic error of ± 0.02 K in the chemical potential. The typical noise in our frequency measurements is ± 5 mHz. As a result the random error in our determination of $\Delta\mu$ is ± 0.01 K.

III. RESULTS

Figure 2 shows a comparison between ^{3}He adsorption and the well understood case of ^{4}He adsorption. There are several things to note. The frequency shift for ^{3}He on Cs diverges upon approaching saturation, just as it does on Au, as shown in Fig. 2(a). This indicates that ^{3}He wets both substrates. However there is a step-like feature near $\Delta\mu = -0.6$ K. This step is absent for ^{3}He on Au, but is qualitatively similar to prewetting steps found for ^{4}He on Cs. Figure 2(b) shows a ^{4}He on Cs prewetting step measured on the same (annealed) Cs substrate used for the ^{3}He measurement shown in Fig. 2(a). The step occurs much farther from saturation and is less steep for ^{3}He than for ^{4}He. The width of the step was reduced approximately by a factor of three upon annealing for ^{3}He. Although a comparison was not made for ^{4}He before and after annealing on the same substrate, ^{4}He prewetting steps are about factor of two narrower on annealed substrates than the prewetting steps found on an unannealed substrate.

The results for ^{3}He adsorption isotherms measured on the second annealed cesium substrate down to ~0.2 K are plotted in Fig. 3. The data have been corrected for frequency shifts due to the pressure and viscosity of the ^{3}He vapor surrounding the microbalance.[9, 10] To prevent the data from overlapping, the data plotted in Fig. 3 are vertically offset. The location of the steps relative to liquid vapor coexistence is nearly constant for all temperatures, but the steps become narrower and steeper as the temperature is lowered.

IV. DISCUSSION

The most salient feature of the data is the thickness steps found for ^{3}He on Cs near $\Delta\mu = -0.6$ K. A question that arises from these measurements is whether these steps are due to first order prewetting transitions or are merely regions of high 2D compressibility in the adsorbed films.

There are two examples of similar adsorption systems for which first order prewetting is firmly established: ^{4}He on cesium[3] and H_2 on rubidium.[4,6] In these systems, first order prewetting was established through the connection of the prewetting line with a first order wetting transition. At temperatures just above the wetting temperature, thermodynamics requires that the steps are first order prewetting transitions. In the case of ^{3}He, since there is no wetting transition, a parallel argument cannot be made and the identification of the steps with prewetting must rely on other features of the data.

A well known signature of first order phase transitions is hysteresis. In order to determine if the ^{3}He/Cs steps were hysteretic a small amount of ^{3}He was admitted to the experiment cell and the temperature was raised and lowered between ~0.35 K and ~0.40 K, so that the chemical potential was swept back and forth over the region of the step. No hysteresis in $\Delta\mu$ larger than the experimental resolution, about 10 mK, was found.

If the steps found in the ^{3}He isotherms at low temperatures are first order transitions, then there should be an indication of a prewetting critical point at higher temperatures. A conventional method used to determine the critical points for phase transitions in 2D systems is to examine the temperature dependence of the inverse steepness of the steps, $(-d\mu/df)$, found in the isotherms.[3,12,13] Figure 4 illustrates this analysis for ^{4}He on annealed cesium as well as a similar analysis of the ^{3}He adsorption data. Figure 4(a) is a plot of the minimum of the derivative $(-d\mu/df)_{\mathrm{min.}}$ from Ref. 3 for ^{4}He adsorption isotherms measured on a cesium plated microbalance similar to the one used for this experiment. Below 2.5 K $(-d\mu/df)_{\mathrm{min.}}$ is very small (corresponding to very steep steps) and nearly constant. Above 2.5 K $(-d\mu/df)_{\mathrm{min.}}$ increases rapidly with increasing temperature. This indicates that the prewetting critical point temperature is $T_c^{pw} \cong 2.5$ K.

For comparison, the same derivative of the ^{3}He data measured on the third annealed cesium substrate is shown in Fig. 4(b). The dependence of the derivative on temperature is qualitatively similar to that for ^{4}He. Below about 0.6 K, the derivative is nearly constant, and at higher temperatures it increases rapidly. This result can also be obtained by a visual inspection of the data of Fig. 3. The four lowest temperature isotherms (measured at temperatures less than 0.6 K) are nearly identical, whereas the steps in the two isotherms measured above 0.6 K are clearly less steep. This behavior is suggestive of a first order prewetting line with a critical point at ~0.6 K.

The results for ^{3}He on annealed Cs are summarized in Fig. 5. The plot shows the positions of the points of maximum slopes from isotherms measured using the first and second annealed cesium substrates. The location of the steps is essentially parallel to the bulk coexistence curve, consistent with the expectation that ^{3}He wets Cs at all temperatures.

A clear difference between the isotherms measured for ^{3}He and ^{4}He is that the steps in the ^{3}He case are ~20 times wider than those found for

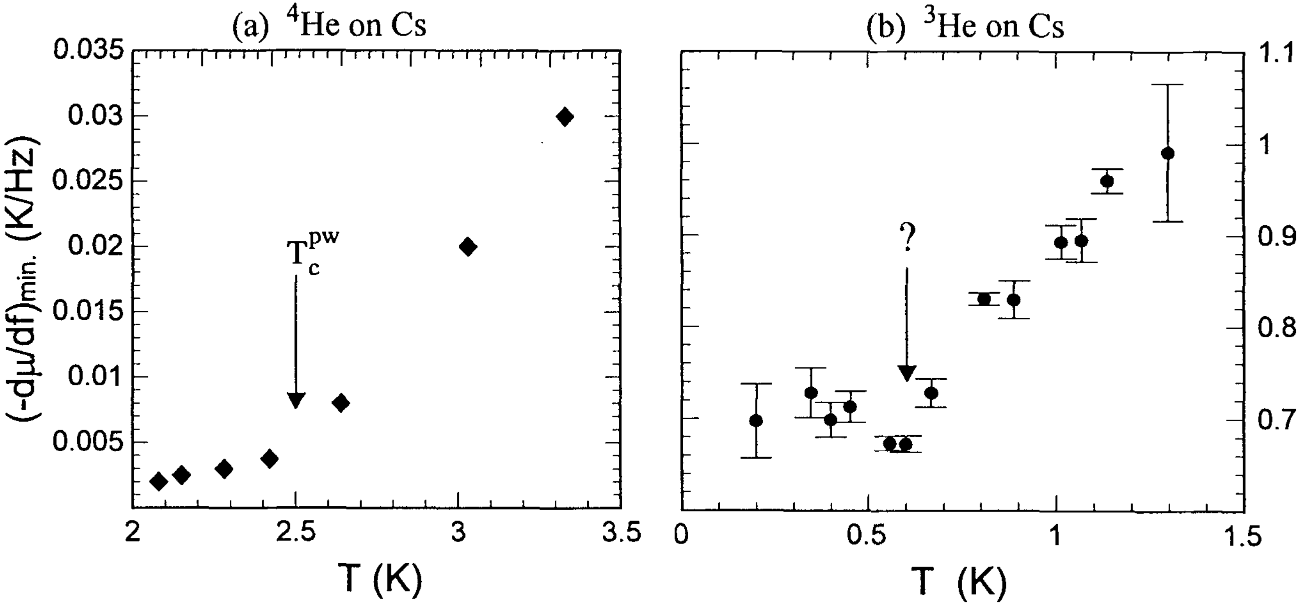

Fig. 4. The minimum of the derivative $-d\mu/df$ plotted as a function of temperature. (a) ^{4}He on annealed Cs, from Ref. 2. $T_c^{pw} \simeq 2.5$ K. The break in slope identifies the prewetting critical point temperature, T_c^{pw}. (b) ^{3}He on annealed Cs. There is a similar break in slope near 0.6 K which is suggestive of a prewetting critical point.

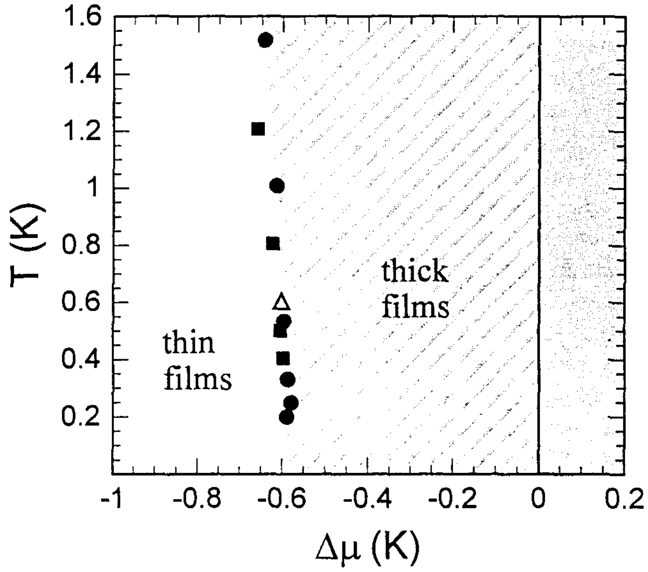

Fig. 5. Summary of the results for ^{3}He on annealed Cs showing the location of the steps measured in adsorption isotherms. The square symbols are data taken with the first annealed Cs surface and the circles are data taken with the second annealed Cs surface. The open triangle indicates the temperature below which the steepness of the steps is constant.

^{4}He.[14] In order to make a convincing argument that the ^{3}He/Cs steps are due to first order prewetting transitions, an explanation must be offered for their large width. A possible cause of the finite width of the steps is residual inhomogeneity of the substrate. To explore the possibility that ^{3}He prewetting might be more sensitive to inhomogeneity than ^{4}He prewetting we considered a simple model of the effect of variation of the substrate potential. Using Eq. (2.5) from Ref. 15 we calculated the effect of a small variation of the depth of the substrate potential (the parameter D from Ref. 15) on the location of the prewetting step. The results indicate that first order prewetting steps should be broadened by about the same amount for both ^{3}He and ^{4}He on Cs. Therefore, this type of inhomogeneity cannot explain our results.

In an attempt to experimentally explore the effect of inhomogeneity we measured isotherms of ^{3}He and ^{4}He on both annealed and unannealed substrates. As a result of annealing, the steps found for both ^{3}He and ^{4}He became sharper, and were shifted to lower chemical potentials, but the maximum slopes of the steps were left relatively unchanged.

Pricaupenko and Treiner (PT)[7] have made predictions of the adsorption behavior of ^{3}He on cesium at $T = 0$ K. In their theory the Fermi statistics of the ^{3}He dictates the wetting behavior. They have predicted quantum prewetting transitions which are driven by the successive filling of 2D Fermi disks at the surface. In addition to a large prewetting transition, this theory predicts a series of smaller film thickness transitions between the prewetting transition and bulk coexistence.

The calculations of PT predict a prewetting transition for ^{3}He on Cs at $\Delta\mu \cong -0.2$ K. The data show a step at $\Delta\mu \cong -0.6$. This disagreement seems significant because the parameters describing the substrate potential used in the model were adjusted to give a correct result for the calculated wetting temperature of ^{4}He on Cs.

A careful search for any sign of the predicted secondary film thickness transitions was done at $T = 0.295$ K using the second annealed cesium surface. The results are shown in Fig. 6. The graph of Fig. 6(a) shows the adsorption isotherm plotted as $-\Delta f$ for the cesium plated microbalance vs. $-\Delta f$ for the gold plated microbalance. The open circles are the data and the solid line is a second order polynomial fit to the data in the range $1 < -\Delta f\,(\text{gold}) < 1.4$. To uncover any small features of the data that may be obscured by the steeply sloped background we subtracted the fitted curve from the data. The results are shown in Fig. 6(b). One large step is clearly evident in both graphs but no other features can be found in the data. To see if this analysis would have detected secondary thickness transitions, a calculated isotherm taken from Fig. 3 of Ref. 7 was blurred to give the prewetting step a width approximately equal to that found in the measured steps. This calculated isotherm was then analyzed using the same method as is shown in Fig. 6. The results showed that if secondary thickness transitions were present in the experimental data, they should have been revealed by this analysis even if they were smeared to a width similar to that of the measured steps. Since no evidence for the secondary transitions was found in the data we conclude that they do not occur in the ^{3}He/Cs system for temperatures greater than 0.3 K.

In conclusion, ^{3}He is found to wet cesium at all temperatures. The measured isotherms show very little adsorption until a chemical potential about 0.6 K below saturation where there are step-like features. We have explored the possibility that these steps may be due to first order prewetting transitions by analyzing the width and steepness of the steps. Because of the lack of a natural scale of steepness it is difficult to come to a definitive conclusion on this point. A similar problem plagues the comparison between theory and experiment. Extraordinarily long relaxation times have limited our measurements to temperatures above 0.2 K, but the theory applies strictly at $T = 0$ K. If in fact the theory is applicable only for temperatures for which monolayer thick film are degenerate, temperatures in the low mK ranged would be required.[16] Therefore, a conclusive

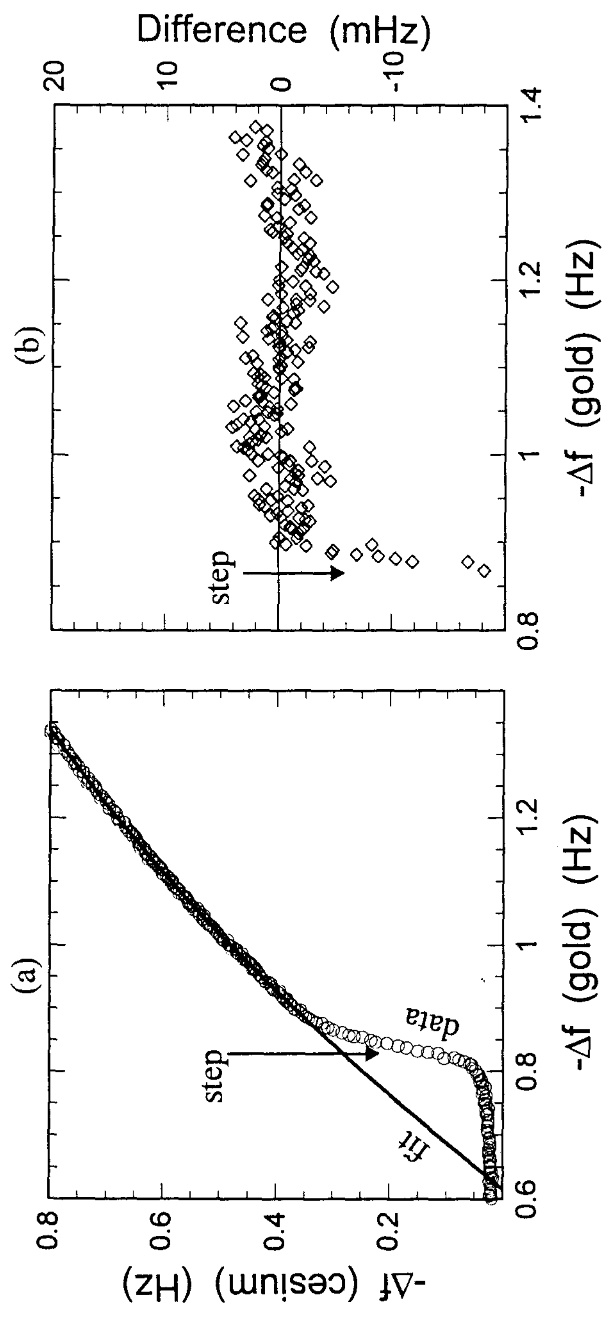

Fig. 6. Search for secondary film thickness transitions. (a) Adsorption isotherm at $T \geq 0.295$ K, plotted as $-\Delta f$ for the cesium plated microbalance vs. $-\Delta f$ for the gold plated microbalance. The open circles are the data and the solid line is a fit to the data as described in the text. (b) The data from (a) with the fitted curve subtracted.

confrontation between theory and experiment will require a calculation of finite temperature effects.

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