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Wetting Transitions of Liquid Helium on Oxidized Rubidium Metal Surfaces

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Prewetting transitions of liquid helium on rubidium surfaces exposed to increasing quantities of oxygen have been observed. They reveal a decrease of the wettability of the surface. A state has been reached where the rubidium surface appears non wetted for temperatures below 1.45 K. The dewetting transition has been observed.

1. INTRODUCTION

Heavy alkali metals are weak binding substrates for helium atoms.[1] Because of the particularly low work function of those metals, the electronic density extends farther from their surface and repels efficiently the helium atoms. As a consequence, their surfaces are either non wetted or only weakly wetted by liquid helium,[2,3] giving the opportunity to observe wetting and prewetting transitions.[4,5,6] Because alkali suboxides have work functions significantly lower than the pure metals, it has been argued recently[7] that limited oxidization of those surfaces should make them even less binding, and accordingly less wettable by liquid helium. Some first experimental evidences have also been reported.[7]

The aim of this paper is to report on the observation of prewetting transitions on rubidium surfaces exposed to increasing quantities of oxygen. A state has been reached where the rubidium surface appears non wetted for temperatures below 1.45 K. The dewetting transition has been observed.

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2. EXPERIMENTAL PROCEDURE

The experiments are performed using the methods described in references.[5,7] The design of the cell is shown in Fig. 1. It is filled with helium at a pressure about 0.9 bar at liquid nitrogen temperature. This should be enough to provide a saturating film on all the wettable surfaces up to 1.9 K. However, there is some uncertainty about the final pressure in the cell after its sealing off. Bulk rubidium metal is shaped to form a ring on the inner surface of the bulb prepared in the upper part of the cell. A capillary (*cap*) allows one to drive this upper compartment off saturation by a heating power $\dot{Q}_l$ on the order of 30 μW. Chemical potential offsets $\Delta\mu$ up to -80 mK are sufficient to produce the prewetting transition on pure rubidium.

The thick or thin state of the helium film over the rubidium surface is deduced from the thermal resistance $R_{th}=(T_3-T_2)/\dot{Q}_h$ of the part of the tube containing the rubidium. When the rubidium is dry (which means covered by an atomically thin film, most probably a 2D gas[8,9]), a thermal resistance in the mK/μW range arises at each border between the rubidium

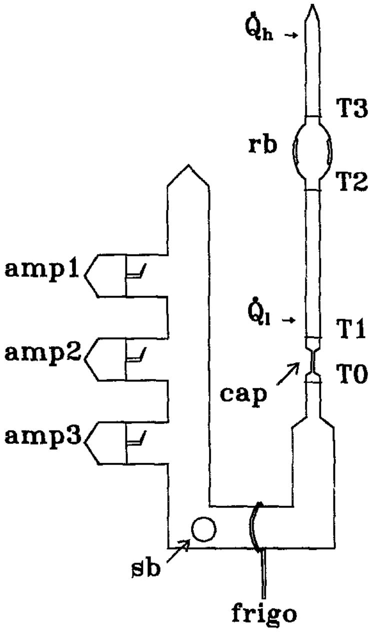

Fig. 1. The experimental cell. It is filled with 0.9 bar of helium at liquid nitrogen temperature. *rb* = rubidium metal ring, *amp* 1, 2, 3 = ampoules containing different quantities of oxygen gas, *sb* = steel ball to break pig tails.

surface and the thick helium film on the nearby glass surface. Conversely when the thick film extends from each border over the rubidium surface, a low thermal resistance path exists for the heat flow from the upper thick film to the lower one via the rubidium metal. The larger the overlap, the lower the thermal resistance. The total thermal resistance is the sum of the two contributions from each border.

Three ampoules (*ampl*,...) containing various quantities of oxygen are isolated from the main cell by pig tails. By breaking them with the steel ball *sb* at room temperature, their content is introduced in the main cell to oxidize the rubidium metal. The area of the metal surface is typically 2.5 cm^2. Ideally, 6 nmoles of oxygen represent a mono layer on such a surface, whereas about 1 mmole would be necessary to completely oxidize the bulk metal. The exact oxidization stage of the active surface reached with a given amount of oxygen introduced in the cell is difficult to estimate. The microscopic area could be larger than 2.5 cm^2 and the oxidization process may affect more than one layer of the metal. Some rubidium may also be present elsewhere on the glass surface, which can capture part of the oxygen. Furthermore, the oxygen molecules reach the rubidium surface by diffusing at room temperature through the helium gas present the cell. Besides slowing down the oxidization process, this results in an exposure of the rubidium surface which decreases from the bottom to the top of the ring. Oxygen is more likely to reach the rubidium surface near the bottom of the ring than near the top. For a height of the ring equal to its diameter (this is the actual situation), a numerical simulation shows that the top edge receives about hundred times less oxygen than the bottom one. This means that introducing an amount of oxygen in the cell as large as 100 nmoles leaves the upper edge practically unaffected.

3. PREWETTING TRANSITIONS

In Fig. 2a, the prewetting transition on pure rubidium at $T = 1.44$ K is presented for reference. The offset from saturation is measured using the scale $(-\Delta\mu)^{2/3}$. This scale is convenient because it is approximately proportional to the variation of the spreading power of the thick film.[5] The prewetting transition manifests itself by a change of the thermal resistance from a negligible value to a finite value of the order of 2.5 mK/μW. This change is hysteretic. The drying and wetting thresholds, which can be identified as the points where the thermal resistance becomes no zero, are separated by a distance on the order of 4 mK$^{2/3}$ on the scale $(-\Delta\mu)^{2/3}$. Their mean value, 9 mK$^{2/3}$, is close to the previous results obtained on rubidium.[5]

In Figs. 2b-d, the various shapes of the transition for increasing amounts of oxygen are shown, at about the same temperature. The evolution

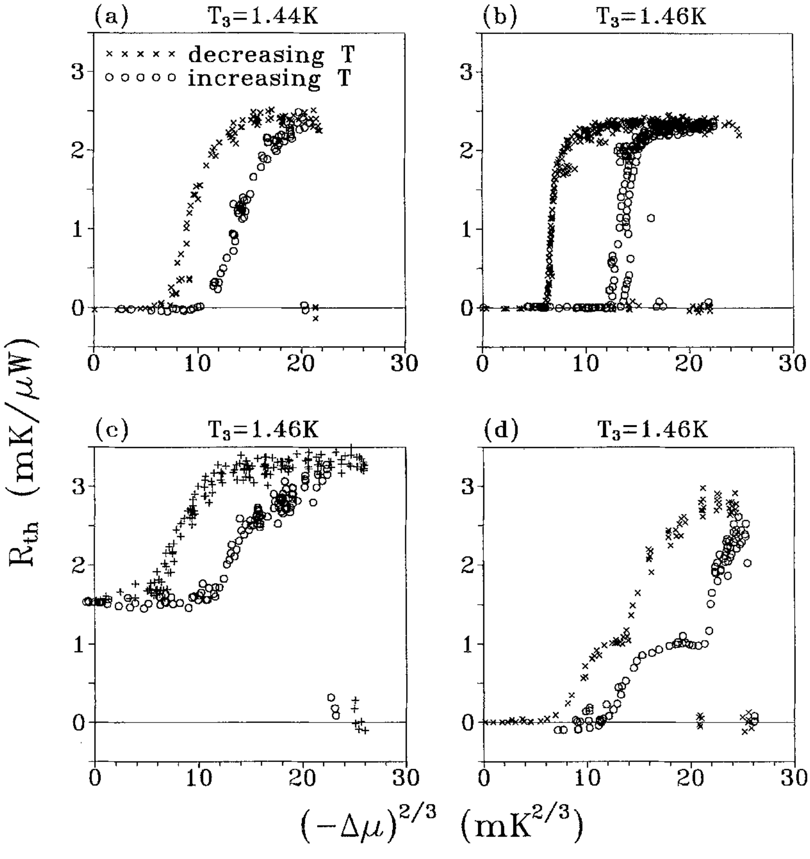

Fig. 2. Prewetting transitions on the rubidium surface for increasing exposure to oxygen. $\Delta\mu$ is the offset from the saturation chemical potential. $(-\Delta\mu)^{2/3}$ is approximately proportional to the variation of the spreading power of the thick film. (a) pure metal (b) with 60 nmoles of oxygen (c) with 85 nmoles of oxygen (d) with 120 nmoles of oxygen.

begins by a widening of the cycle on its left side, along with a steepening of the cycle sides (Fig. 2b). Then part of the cycle shifts to the left until it disappears (Fig. 2c). The thermal resistance is finite at saturation, its value 1.5 mK/μW being about half the maximum value. This indicates a non wetted situation. A transition remains for the other half, roughly at the same place as the original transition. In the final state shown in Fig. 2d, the thermal resistance is again zero at saturation. A first transition occurs at the original position, and a second one lies farther, at about 18 $mK^{2/3}$.

A plausible interpretation of these data relies on the hypothesis that only the lower border of the rubidium ring is significantly oxidized, for the reason explained in Section 2. Thus, the contribution of the upper border of the ring to the thermal resistance remains unaffected by oxygen and gives rise to the transition centered around 9 $\mathrm{mK}^{2/3}$. The transition corresponding to the lower border undergoes a non monotonic change with the increasing oxidization. It is first shifted towards lower unsaturation, revealing a less wettable substrate, until the situation of non wetting is reached. The final state indicates a substrate more wettable than the pure metal surface. This evolution is to be compared with that of the work function of heavy alkali surfaces under oxidization.[11, 12, 13] For cesium, a significant lowering of the work function is reached as the oxidized metal near the surface reaches the stechiometry Cs_3O_{11}. For larger proportion of oxygen, the work function increases again and reaches a final value larger than that of the pure metal. Hence the correlation between the wettability of alkali surfaces with their work function is at least qualitatively confirmed.

4. WETTING TRANSITION

At saturation, a transition has been observed from the wetted state found at higher temperatures to the non wetted situation illustrated in Fig. 2c at $T = 1.46$ K. The thermal resistance rises to a finite value for temperatures lower than 1.5 K (see Fig. 3). This reveals a dewetting transition. The smooth rise at lower temperatures can be accounted for by the variation of the glass thermal conductivity. When the temperature is increased from 1 K, the thermal resistance remains finite up to 1.76 K. Because the thermalisation time constant becomes very long at higher temperatures, it was difficult to measure reliably the thermal resistance. Thus the wetting transition could not be observed. It lies presumably at higher temperatures. As on cesium surfaces,[14] the wetting transition exhibits a strong hysteresis. In the cesium case, the hysteresis width is about 16 K/Å^2, measured on the appropriate scale $\sigma_{lv}(0) - \sigma_{lv}(T)$, which is approximately proportional to the variation of the spreading power of the thick film. If one assumes the same width in the present case, one would expect the wetting transition to be located at $T = 1.74$ K, very near the maximum temperature for which a measurement could be achieved.

Among the difficulties encountered at higher temperatures, it was found that the temperature fluctuations of the cell cause apparent changes in the measured thermal resistance. When the temperature is raised or lowered, transient decreasing or increase of $T_3 - T_2$ is observed. This effect is attributed to the energy needed to adjust the helium vapor density above the ring. If the temperature increases, an extra heat has to flow through the ring towards the upper part of the cell in order to vaporize a fraction of the film to produce the larger vapor density. This heat flow is subtracted from

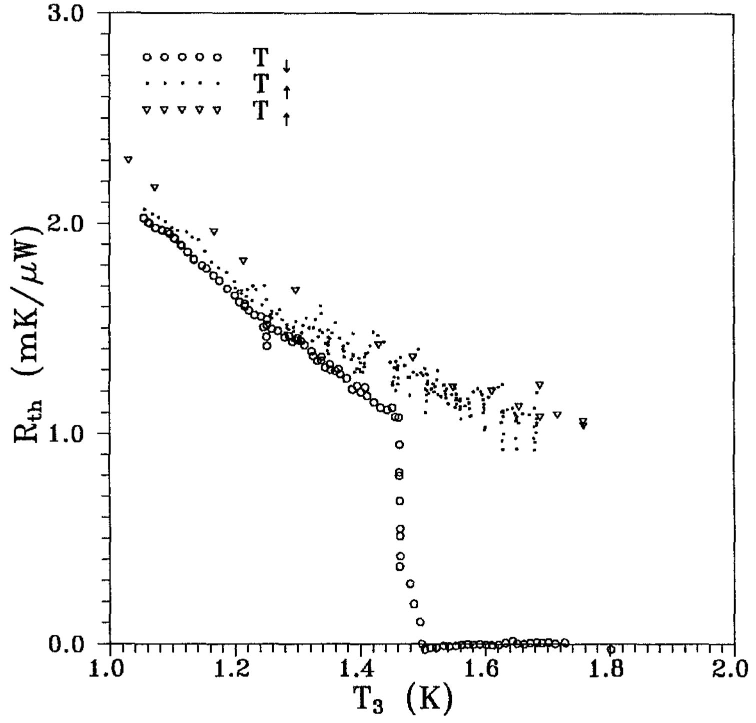

Fig. 3. Dewetting transition observed on the oxidized rubidium surface corresponding to Fig. 2c when the temperature is lowered (open circles). The wetting transition could not be observed by increasing the temperature up to $T \simeq 1.76$ K (dots and triangles). It lies presumably at higher temperatures.

$\dot{Q}_h$ until a new equilibrium is reached, producing a decrease of $T_3 - T_2$. This effect increases strongly with the temperature, following the vapor pressure. Some of the data of Fig. 3 taken while the temperature was changing, have been corrected for this effect.

CONCLUSION

We have shown that a partially oxidized rubidium surface can exhibit wetting properties close to that of cesium. A dewetting transition have been observed at 1.5 K. The optimum oxidization stage of rubidium has not been determined. The suggested correlation between the work function and the wetting properties for helium may be used as a guide for that, but its experimental determination would require films of metal uniformly exposed to oxygen. This is not feasible in our experiment, but could be done in quartz micro balance experiments. Another strategy would be to produce bulk suboxides as shown by Simon.[15] Hysteresis in the wetting and prewetting transitions is confirmed to be present for these particular substrates, as for pure metals.

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