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Investigation of the Effect of Oxygen Impurities on the Wetting Properties of Alkali Metal Surfaces by Liquid Helium.

B. Demolder, F. Raad and J. Dupont-Roc

Laboratoire Kastler Brossel,[†] *Département de Physique de l'Ecole Normale Supérieure, 24 rue Lhomond, 75231 Paris Cedex 05, France*

The weak binding properties of heavy alkali metal surfaces for helium have been related to their metallic nature and their particularly small work function. A natural consequence would be that oxidized surfaces should loose their non wetting properties for liquid helium. It is pointed out that the special oxidization process of these metals could unexpectedly lead to an opposite result at some intermediate stage. First experimental results on rubidium shows evidences for such an effect.

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1. INTRODUCTION

The study of Zaremba and Kohn[1] showed that heavy alkali metals are weak binding substrates for helium atoms. Cheng *et al.*[2] predicted from this property that the surface of some of those materials should be non wetted by liquid helium at $T=0$. Subsequent experiments[3] proved that this is indeed true for cesium up to $T=2$ K,[4] whereas rubidium is just about the limit of non wetting at $T=0$.[5,6] Cesium being the heaviest stable alkali metal, it appeared up to now as providing the only surface non wetted by liquid helium. At first sight, any impurity on the surface should increase its wettability.

The aim of this paper is to put forward the idea that a small amount of oxygen can on the contrary make the alkali metal surfaces less wettable

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[†] Laboratoire de L'Ecole Normale Supérieure et de L'Université Pierre et Marie Curie, associé au CNRS (URA 18)

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by liquid helium, and to report some first results of experiments made on rubidium, which support this conjecture.

2. THE WORK FUNCTION OF METALS AND THEIR WETTING PROPERTIES FOR LIQUID HELIUM

Table 1 lists the characteristics of alkali metal surfaces, as computed in reference ([1]). C_3 is the Van der Waals coefficient of their long range interaction with a helium atom, D is the well depth for the same potential. The last column provides the opposite of the surface grand potential $\Omega_s^{(\text{thick})}(0)$ for a thick helium film, at saturation and T=0. It is computed according to the model discussed in this same issue.[7] The substrates for which this parameter is negative are predicted to be wetted at $T = 0$. The parameter $-\Omega_s^{(\text{thick})}$ is equal to the spreading power at $T = 0$, and it provides a measure of the wettability of the substrate. It can be noticed that the work function W of the metals varies in the same way as their wettability. This has been interpreted[3] as resulting from the strong repulsion of the helium atoms by the electrons in the metal.[1,8] The wavefunction of the conduction electrons of the metals extends outside its surface. The electronic density ρ_e decays as

$$\rho_e \simeq \exp(-2z\kappa) \tag{1}$$

where κ is related to the work function W by

$$W = \frac{\hbar^2\kappa^2}{2m_e} \tag{2}$$

Hence for substrates with small W, the electrons spill further out of the metal and repell more strongly the helium atoms. This results in shallower potential wells and less wettable substrates.

The oxidization of heavy alkali metals is a complex process, in which various types of suboxides, peroxides and hyperoxides appears at interme-

Table 1
Characteristics of alkali metal surfaces[1]

metal	W eV	C_3 (KÅ^3)	D K	$-\Omega_s^{(\text{thick})}(0)$ K/Å^2
Cs	2.14	672.8	4.4	-0.31
Rb	2.21	754	5.0	-0.27
K	2.39	812	6.3	-0.19
Na	2.70	1067.2	10.4	0.05
Li	3.10	1357.2	17.1	0.41

diate stages. Furthermore, it has been noticed, especially for cesium, that the electronic properties of the surface changes during this process. For an exposure below 0.3 L (1 L=1 langmuir=10^{-6} Torr × s $\simeq$ 2.5 nmol/cm^2), apparently nothing happens. For further exposure to oxygen, the work function decreases from 2 eV to 1.3 eV, a minimum value reached for about 1 L. Finally, W increases again, up to values larger than the initial one, for exposures larger than 3 L. The beginning of this last stage is accompanied by spontaneous emission of electrons by the surface (exoelectrons). Tentative explanations for those various phenomena may be found in reference (^{9,10}).

The fact that the work function W is significantly reduced by an exposure of the surface to about 1 L of oxygen is particularly interesting for the wetting properties of this surface by liquid helium. The correlation between W and the wettability discussed above suggests that a proper exposure to oxygen could make the oxidized surfaces less wettable than the pure metal. A bold extrapolation from the data of Table 1 suggests that an oxidized cesium surface would be as different from pure cesium as cesium is from sodium. This would suggest a value of $\Omega_s^{(\text{thick})}$ larger than that of cesium by about 0.3 K/Å^2. This is a huge quantity, comparable to the liquid surface tension of helium 0.274 K/Å^2. This suggests that it could be wetted only near helium critical point. Similarly, oxidized rubidium would be much more non wettable than pure cesium surface. Of course such an extrapolation is purely empirical and should be supported by realistic models for electronic properties of the oxidized surfaces and for their interaction with helium. But it suggests an effect sufficiently large to be worthy of an experimental test.

3. EXPERIMENTAL PROCEDURE

The experiments are performed on rubidium surfaces using the methods described in reference (^{5}). The design of the pyrex cell is shown in figure 1. It is filled with helium (about 2 bar at room temperature) which condenses below 1.8 K to provide a saturating film on all the wettable surfaces. Bulk rubidium (rb) 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. They are deduced from the measurement of the temperature difference $T_1 - T_0$. 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 (thin film state), a thermal resistance on the order of a few mK/μW arises at each border between the rubidium

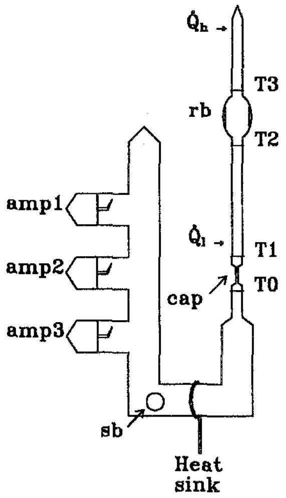

Fig. 1. Design of the experimental cell

surface and the thick helium film on the nearby glass surface. For each temperature T, the chemical potential offsets for the prewetting transition $\Delta\mu_{\mathrm{pw}}$ is determined. This provides the prewetting line, which is plotted using the coordinates $\sigma_{lv}(0) - \sigma_{lv}(T)$ and $(-\Delta\mu_{\mathrm{pw}})^{2/3}$ in order to have nearly a straight line. Furthermore $(-\Delta\mu_{\mathrm{pw}})^{2/3}$ is, in a first approximation, a linear function of $-\Omega_s^{(\mathrm{thick})}(0)$. Thus, at a given temperature, it is a convenient measure of the surface wettability. Two or three ampoules (amp1, ...) containing various quantities of oxygen are isolated from the main cell by pig tails which can be broken by a steel ball (sb).

The surface of the pure rubidium was first studied and the prewetting lines was found in reasonable agreement with an earlier determination,[5] although flow instabilities in the capillary prevented us to get consistent data below 1.3K. Then one pig tail was broken and its oxygen content diffused through the helium gas into the cell. However, the capillary slows down considerably the penetration of oxygen into the upper part of the cell containing the rubidium surface. To speed up the process, this part was alternatively diped into liquid nitrogen and warmed up, forcing the gas to flow between the two parts of the cell. Then the prewetting transition was determined again on the oxidized surface, and so on.

For the third ampoule (amp3) containing a relatively large quantity of oxygen, the above procedure was not applied. The oxygen was let to diffuse

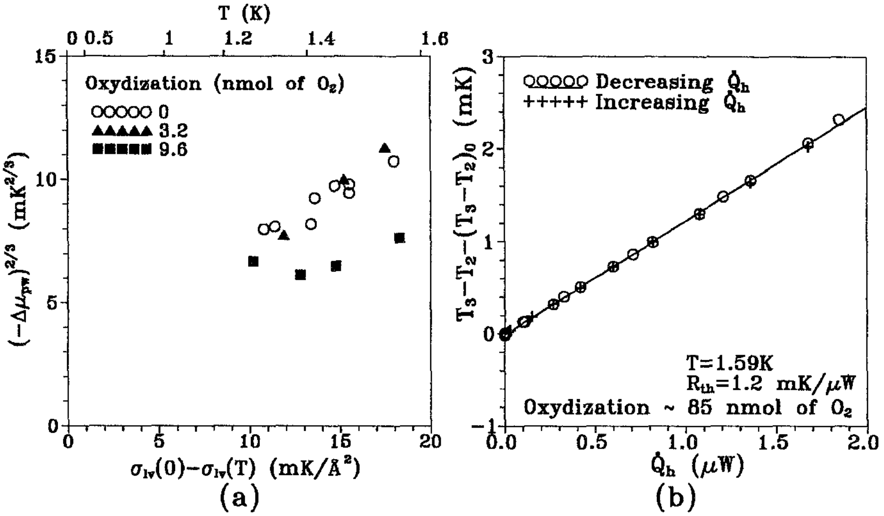

Fig. 2. (a) Prewetting lines for three different amounts of oxygen. (b) Evidence for a finite thermal resistance between T_3 and T_2, indicating a non wetted rubidium surface at T=1.6 K. The contribution of thermometer offsets $(T_3 - T_2)_{\dot{Q}_h=0}$ to $T_3 - T_2$ has been substracted out.

through the capillary for one or two days. The process was then blocked by cooling down the sample below 4K, and the wetting properties were studied. Then more oxygen was allowed to diffuse into the upper part for a day, and so on. Note that with this last procedure the lower part of the rubidium ring surface is likely to be more oxidized than the upper part, because of the oxygen diffusion from below.

The macroscopic surface of the metal is typically 2.5 cm^2, so that the optimal exposure to oxygen amounts to 6 nmol. However, microscopic quantities of rubidium may also be present on the glass surface, which can thus capture a significant amount of oxygen. Hence the optimal exposure is the minimum quantity to introduce. In fact one order of magnitude larger may be necessary.

4. RESULTS AND COMMENTS

Successive prewetting lines are presented in Figure 2a. The quantity of oxygen first introduced was about 3 nmol. No significant change appears. The second amount added was about twice larger. A shift about −3 mK$^{2/3}$

was observed for $(-\Delta\mu_{\rm pw})^{2/3}$, indicating a less wettable substrate. This shift is smaller than the uncertainty ± 4 mK$^{2/3}$ on the location of the prewetting transition due to the existence of the hysteresis cycle as function of $(-\Delta\mu)^{2/3}$. But the relative displacement and the distortion of the hysteresis cycle is significant. It suggests that the two borders of the rubidium are no more identical. Then, by introducing more oxygen from amp3, we observed a very spectacular effect. A finite thermal resistance across the rubidium was observed at saturation, up to $T = 1.6$K, indicating a non wetted state of the rubidium surface. This is shown in Figure 2b. The order of magnitude of this resistance is consistent with one non wetted rubidium border, presumably the lower one.

This first results open interesting possibilities. First, it suggests that for cesium surfaces, large contact angles can be obtained. Second, other alkali metal such as rubidium can be made non wetted by liquid helium. Sodium should be tested in the same way. It is also a warning for the studies concerning the wetting properties of the pure metal surfaces : the cleanest surfaces are *not* the less wetted ones.

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