

## The Solid-Liquid Surface Tension at a Helium/Cesium Interface

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*The existence of a wetting transition for helium adsorbed on cesium provides an experimental opportunity to investigate the solid-liquid surface tension. We have extracted the temperature dependence of the solid-liquid surface tension at the  $^4\text{He}/\text{Cs}$  interface from our earlier measurements of the wetting temperature of pure  $^4\text{He}$  on thin layers of cesium overlaying gold. More recently we have measured the wetting temperature as a function of the  $^3\text{He}$  concentration for  $^3\text{He} - ^4\text{He}$  mixtures. An analysis of these experiments paralleling Andreev's investigation of the free surface reveals  $^3\text{He}$  bound states at the helium/cesium interface.*

It is now well known that both pure  $^4\text{He}^1$  and  $^3\text{He}-^4\text{He}^{2,3}$  mixtures display first order wetting transitions on Cs surfaces. Wetting transitions are driven by surface tensions. At a first order wetting transition

$$\sigma_{sl}(T_W) + \sigma_{lv}(T_W) - \sigma_{sv}(T_W) = 0. \quad (1)$$

Here the  $\sigma_{\alpha\beta}$  are surface tensions,  $s, l$ , and  $v$  are solid, liquid and vapor, respectively. Since for pure  $^4\text{He}$  and for  $^3\text{He} - ^4\text{He}$  mixtures, the liquid vapor surface tension is well known,<sup>4,5</sup> a measurement of the wetting temperature determines  $\sigma_{sl} - \sigma_{sv}$ . This quantity is nearly inaccessible by other experimental techniques.

We have measured the wetting temperature of pure  $^4\text{He}$  on compound substrates consisting of Cs overlayers on effectively semi-infinite Au.<sup>6</sup> As the Cs overlayer becomes thinner, the adsorption potential of these structures becomes stronger and the wetting temperature decreases. With the aid of a simple model for the adsorption potential<sup>7</sup> we can extract the temperature

dependence of  $\sigma_{sl}$  from the measurements. The results can be interpreted by a model of  $\sigma_{sl}$  that uses the liquid-vapor surface tension as a starting point and accounts for the differences between the surface excitations at the free and the substrate surfaces. We have also measured the wetting phase diagram of  $^3\text{He} - ^4\text{He}$  mixtures<sup>3</sup> and extracted the solid-liquid surface tension as a function of  $T$ , the temperature, and  $X_3$ , the  $^3\text{He}$  concentration. An analysis of these results patterned on Andreev's treatment of the liquid-vapor surface tension<sup>9</sup> reveals  $^3\text{He}$  bound states at the He/Cs interface. These bound states were anticipated theoretically<sup>10</sup> and exist because the weak adsorption potential of the Cs surface does not strongly compress the liquid.

In the Cs overlayer experiment, the Cs thicknesses varied between roughly 2 and 20 layers, and the wetting temperatures varied between about 1.5 K and 2.1 K. Here we will describe how those measurements can be used to extract the temperature dependence of  $\sigma_{sl}$  and suggest a model that accounts for it. Our approach seems appropriate for the uncompressed helium films on a weak binding surface.

For each Cs thickness the adsorption potential enters Equation 1 as a contribution to  $\sigma_{sl} - \sigma_{sv}$ . One of the central results of the paper that predicted the nonwetting of helium films on the alkali metals<sup>11</sup> is that to a high degree of accuracy

$$\sigma_{sl}(0) - \sigma_{sv}(0) = \sigma_{lv}(0) + \int_{z_{min}}^{\infty} \rho(0)V(z)dz, \quad (2)$$

where  $\rho(0)$  is the density of liquid helium and  $V(z)$  is the adsorption potential. The lower integration limit is the minimum in the adsorption potential. For the case of a Cs overlayer on Au,

$$V(z) = V_{Cs}(z) - V_{Cs}(z+d) + V_{Au}(z+d); \quad V_{\alpha}(z) = \frac{4C_{\alpha}^3}{27D_{\alpha}^2} \frac{1}{z^9} - \frac{C_{\alpha}}{z^3}. \quad (3)$$

In Equation 3,  $d$  is the thickness of the Cs overlayer, and  $C_{\alpha}$  and  $D_{\alpha}$  are the van der Waals coefficient and well depth of the adsorption potential presented by a half space of metal  $\alpha$ . At finite temperature we neglect the temperature dependence of  $\sigma_{sv}$  and write

$$\sigma_{sl}(T) - \sigma_{sv}(T) = \delta\sigma_{sl}(T) + \sigma_{sl}(0) - \sigma_{sv}(0). \quad (4)$$

On substitution of Equations 2, 3, and 4, Equation 1 can be solved for  $\delta\sigma_{sl}(T_w)$ . We assume that  $\delta\sigma_{sl}(T)$  is independent of the adsorption potential. This is reasonable because the adsorption potentials for all values of  $d$  in our experiment<sup>6</sup> are quite weak and the differences between them are not large on the scale of the difference between the He-He and Cs-He adsorption potentials.

The five solid symbols in Figure 1 show the result of applying this analysis to the data of Reference 6. The values used for the van der Waals coefficients in Equation 3 are  $C_{Au} = 3181 \text{ KA}^3$ ,  $C_{Cs} = 673 \text{ KA}^3$ ,  $D_{Au} = 92.9 \text{ K}$ , and  $D_{Cs} = 7.4 \text{ K}$ . Except for the last one these are standard values of the adsorption parameters.<sup>12</sup> We have chosen  $D_{Cs}$  to make the values of  $\delta\sigma_{sl}$  trend toward 0 as  $T$  goes to 0. Varying  $D_{Cs}$  by a few degrees shifts each point along the vertical axis but does little to the general slope of the data. Hence the strong temperature dependence of  $\delta\sigma_{sl}(T)$  seen in Figure 1 is not an artifact of the choice of this parameter.

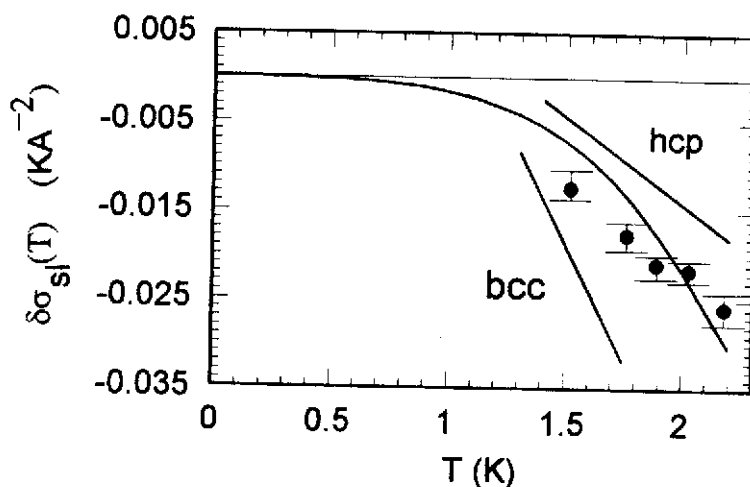


Fig. 1. The temperature dependence of the solid-liquid surface tension on Cesium, data points, and solid  $^4\text{He}$ . The solid curve through the data is discussed in the text.

Other experiments tend to confirm the strong temperature dependence of  $\delta\sigma_{sl}$  that we report. The solid-liquid surface tension of pure  $^4\text{He}$  was measured several years ago at two other weak binding substrates, hcp and bcc solid  $^4\text{He}$ .<sup>8</sup> The temperature dependence on solid  $^4\text{He}$  is roughly linear. As shown in Figure 1, the temperature dependence of  $\sigma_{sl}$  on solid  $^4\text{He}$  is comparable to our results for a Cs surface. Secondly, the adsorption potential parameters and Equations 2 and 3 can be used to predict the low temperature contact angle for  $^4\text{He}$  on Cs. The result is  $46^\circ$ , in near agreement with the value of  $53^\circ \pm 6^\circ$  reported by Wyatt at this Symposium. Wyatt's result suggests a slightly stronger temperature dependence than we infer from our experiment.

Because of the scatter in our results for  $\delta\sigma_{sl}(T)$  and our need to extrapolate these results, we have constructed a physical model of the solid-liquid

surface tension that is consistent with our measured results. In general both surface excitations and contributions from the bulk determine the surface tension. At the free surface<sup>4</sup> and at the solid <sup>4</sup>He - liquid <sup>4</sup>He interface bulk contributions to the surface tension account for a substantial fraction of the temperature variation.

Although there seems to be no quantitative understanding of the bulk contributions effects, they must be included in any reasonable model of  $\delta\sigma_{sl}(T)$ . Density functional calculations show that the density profile near a Cs surface is not far perturbed from its profile at the free surface.<sup>13</sup> Consequently we expect the bulk contribution to  $\sigma_{lv}$  to be a reasonable approximation to the bulk contributions to  $\delta\sigma_{sl}(T)$ . In our model we take explicit account of the differences in the surface excitations at the free and substrate surfaces by replacing the ripplon contribution,<sup>4</sup> which varies as  $T^{7/3}$ , with a contribution from the relevant Rayleigh waves,<sup>13</sup> which varies as  $T^3$ . The result is

$$\delta\sigma_{sl}(T) = \sigma_{lv}(0) - \sigma_{lv}(T) + 6.07T^{7/3} - 0.96T^3 \quad (5)$$

We use the data of Reference 4 for the liquid vapor surface tension and the constants in the surface excitation terms are taken from References 4 and 13. The units are  $\text{erg/cm}^2$ . The results of this model are shown as the solid curve in Figure 1.

We have recently measured the wetting phase diagram of <sup>3</sup>He - <sup>4</sup>He mixtures on thick Cs. The results of these measurements are shown as the data points in Figure 2. This phase diagram shows the recntrant wetting predicted by Pettersen and Saam.<sup>14</sup> The low temperature branch has been previously mapped.<sup>2</sup> Thermodynamics relates the effect of dissolved impurities on the surface tension to the surface excess of the impurity.<sup>15</sup> A positive surface excess decreases the surface tension by an amount that is proportional to the surface excess. A surface deficit of the impurity increases the surface tension. Thus measurements of the effect of <sup>3</sup>He on  $\sigma_{sl}$  can reveal bound <sup>3</sup>He states at the He/Cs interface.

Surface tension measurements at the free surface of <sup>3</sup>He - <sup>4</sup>He mixtures show that there is a positive <sup>3</sup>He surface excess there. According to Andreev,<sup>9</sup> a positive surface excess at the free surface can only result from bound <sup>3</sup>He surface state at the interface.<sup>9</sup> Identical arguments apply to the <sup>3</sup>He surface excess at the He/Cs interface.

Equation 1 can be used to analyze the data in Figure 2. Each surface tension can be written as

$$\Sigma_{\alpha\beta}(T, X_3) = \sigma_{\alpha\beta}(0) + \delta\sigma_{\alpha\beta}(T) + \delta\Sigma_{\alpha\beta}(T, X_3). \quad (6)$$

$\Sigma_{\alpha\beta}(T, X_3)$  is the surface tension at the  $\alpha\beta$  interface of a mixture with bulk <sup>3</sup>He concentration  $X_3$ . The first two terms on the right are the zero temper

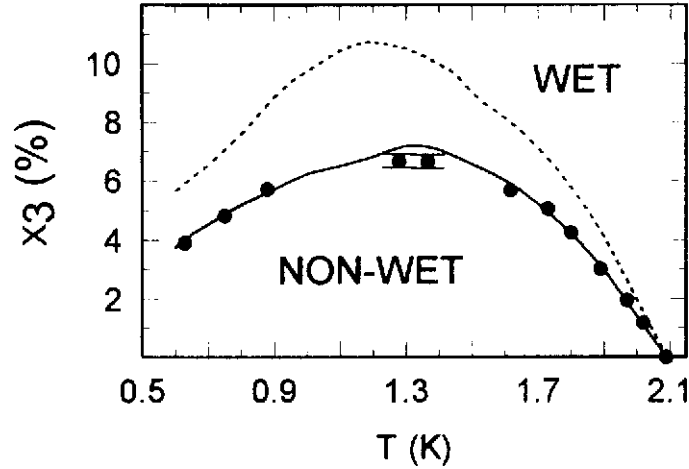


Fig. 2. The wetting phase diagram of  $^3\text{He}$  -  $^4\text{He}$  mixtures on a Cs surface.

ture value and temperature dependence of the pure  $^4\text{He}$  surface tension. The last term is the change in the surface tension due to the  $^3\text{He}$  impurities. We have determined  $X_3$  from the boiling curve data of Sydoriak and Roberts.<sup>16</sup> All of the data were measured on the same Cs substrate, so we may use the pure  $^4\text{He}$  wetting temperature,  $T_W=2.09\text{K}$ , and Equation 1 to characterize the zero temperature values of the surface tensions;

$$\sigma_{sl}(0) + \sigma_{lv}(0) - \sigma_{sv}(0) = -(\delta\sigma_{sl}(T_W) + \delta\sigma_{lv}(T_W) - \delta\sigma_{sv}(T_W)). \quad (7)$$

Upon the substitution of Equations 6 and 7 and neglect of the temperature dependence of the solid-vapor surface tension, Equation 1 can be solved for the change in the solid-liquid surface tension due to the  $^3\text{He}$ :

$$\delta\Sigma_{sl}(T, X_3) = -[\delta\sigma_{sl}(T) - \delta\sigma_{sl}(T_W)] - [\delta\sigma_{lv}(T) - \delta\sigma_{lv}(T_W)] - \delta\Sigma_{lv}(T, X_3). \quad (8)$$

This equation only applies to points along the phase boundary in Figure 2. We have used the data in Reference 4 to evaluate the second term on the right and interpolated measurements of the liquid-vapor surface tension of  $^3\text{He}$ - $^4\text{He}$  mixtures<sup>5</sup> to evaluate the last term. Using Equation 5 to evaluate the first term yields the values of  $\delta\Sigma_{sl}(T, X_3)$  shown as the solid symbols in Figure 3. It is seen that  $\delta\Sigma_{sl}(T, X_3)$  is a negative quantity throughout our temperature range. This is evidence of a positive surface excess of  $^3\text{He}$  and hence a  $^3\text{He}$  bound state at the He/Cs interface. Values of  $\delta\Sigma_{lv}(T, X_3)$  are shown for comparison. It is seen that  $\delta\Sigma_{sl}(T, X_3)$  is about half the size of its free surface counterpart, indicating that there are about half as many  $^3\text{He}$  atoms in the bound state at the Cs substrate as there are in the

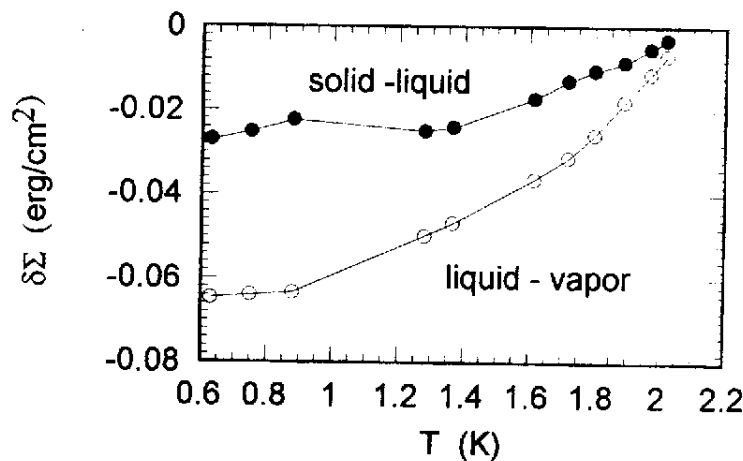


Fig. 3. The change in the surface tensions along the wetting phase boundary, relative to the pure  $^4\text{He}$ , caused by  $^3\text{He}$ .

free surface bound state. The solid curve in Figure 2 is a fit to the wetting phase boundary data characterizing the  $^3\text{He}$  bound state at the Cs surface with a binding energy and effective mass. The best fit, shown in the Figure, gives a binding energy  $1.95 \pm 0.2\text{K}$  below the bulk binding energy and an effective mass of  $0.73 \pm 0.2$  bare masses. The dotted curve in Figure 2 shows the wetting phase boundary in the absence of any  $^3\text{He}$  contribution to  $\sigma_{sl}$ .

The strong temperature dependence of  $\delta\sigma_{sl}$  that emerges from the overlayer experiment is central to interpretation of the mixture experiment. Equation 8 shows that  $\delta\Sigma_{sl}(T, X_3)$  can be written in terms of the differences between the pure  $^4\text{He}$  surface tensions at  $T$  and  $T_W$ . Above 1.5 K, the coldest wetting temperature in the overlayer experiment,  $\delta\Sigma_{sl}(T, X_3)$  can be evaluated without recourse to Equation 5 or any model. The coldest point in Figure 2 at which this can be done is at 1.62 K. Evaluating the first term on the right in Equation 8 by direct linear interpolation of the data points in Figure 1 gives  $\delta\Sigma_{sl}(1.62\text{K}) = -10 \pm 3\text{merg/cm}^2$ , compared to  $-17\text{merg/cm}^2$  when Equation 5 is used. Based only on the overlayer data and the well-established Equation 2,  $\delta\Sigma_{sl}(1.62\text{K})$  is still strongly negative. The existence of the bound  $^3\text{He}$  state at the He/Cs interface is a robust result of our experiment and analysis.

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