Effects of the potential on surface states*

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Surface states are calculated for high-symmetry points in the Brillouin zone of a (001) aluminum film using a pure overlap potential and a Cambridge potential. Results are compared with those of previous calculations to see how surface states are affected by the differences in potential. This comparison shows that behavior of the potential over the last few occupied layers is more important than the way the potential goes to zero outside the jellium edge. Some suggestions are made about the range of validity of the Cambridge model of the potential.

In previous work[1-3] we have calculated energy bands for the (001), (110), and (111) surfaces of aluminum by a new method.[4] Our results differed considerably from the results of an earlier calculation by Boudreaux.[5] Our calculation was most obviously different from Boudreaux's in the treatment of the transition from bulk to vacuum potential. In our calculation we took $V(\overline{G}, z,)$, where $\overline{G}$ is a two-dimensional reciprocal lattice vector, from a superposition of atomic pseudopotentials except for $V(\overline{G} = 0, z)$, where we joined the potential formed by a superposition of atomic pseudopotentials to the self-consistent potential of a jellium slab with the same electron density. Boudreaux used a "Cambridge"[6] potential, i.e., the bulk potential inside the jellium edge and zero outside. Because there may be more than one three-dimensional $\vec{k}$-vector corresponding to a given two-dimensional $\vec{k}$-vector, we suggested that Boudreaux might have omitted some values of $\vec{k}$ from his calculation. Since then Boudreaux has reviewed his notes and concluded that he did not make the suggested error. He has suggested[7] instead that our different results come from the very different methods we have used.

We have repeated our eigenvalue calculation for the high-symmetry points of (001) aluminum. We have used not only a Cambridge potential (which we generated by repeating our $V(\overline{G}, z)$, calculated between $z = \pm \frac{1}{2} a$, out to the jellium surface) but also a simple superposition of atomic pseudopotentials. We have used this latter potential because a self-consistent calculation on (001) lithium[8] gave very different surface states than those previously found from overlapping atomic potentials. We focus here on the results at the $\overline{X}$ point in the two-dimensional Brillouin zone. For aluminum we found $\overline{X}$ surface states in energy gaps both above and below the Fermi energy, whereas Boudreaux found no $\overline{X}$ surface states.

In Fig. 1 we show $V(\overline{G} = 0, z)$ for the three different cases. The film contains 29 occupied layers plus three empty selvage layers on each side. The A planes contain atoms at the cell centers $\vec{r} = (0, 0)$, whereas the B planes contain atoms at the cell corners $\vec{r} = (\frac{1}{2}, \frac{1}{2})$. Note that our previous potential is very much like the Cambridge potential when one is inside the last occupied atomic layer and that our previous potential is more like the pure overlap potential in the way it falls off outside the jellium edge. But the overlap potential falls off much faster over the last few occupied atomic layers than either of the other potentials. Our results for the two new potentials are very much like those previously published. For all three potentials there is a pair of surface states in the band gap at $\overline{\Gamma}$ and in the subband[1] gap at $\overline{M}$. At $\overline{X}$ there is a pair of surface states in the lower band gap and two pairs of surface states in the upper band gap. The symmetries of the Cambridge surface states are the same as the symmetries of our previous surface states. However, for the pure overlap potential the symmetries of the $\overline{M}$ and lower $\overline{X}$ band gap surface states change from $\overline{M}_4^{\pm}$ and $\overline{X}_3^{\pm}$ for our previous potential to $\overline{M}_1^{\pm}$ and $\overline{X}_1^{\pm}$. This represents a shift of charge from the region above B atoms to the region above A atoms since $\vec{r} = (\frac{1}{2}, \frac{1}{2})$ is a nodal line for $\overline{X}_1^{\pm}$ and $\overline{M}_1^{\pm}$, while $\vec{r} = (0, 0)$ is a nodal line for $\overline{X}_3^{\pm}$ and $\overline{M}_4^{\pm}$ states. Figure 2 displays the surface-state wave functions in the lower $\overline{X}$ gap. Because the pure overlap potential is much less attractive in the outer layers, the wave function has its first peak about one layer further inside the crystal than the wave functions for other two potentials. As we have previously discussed[1] $\overline{X}_1^{\pm}$ and $\overline{X}_3^{\pm}$ bulk states are degenerate in the semi-infinite crystal differing only by a translation from an A plane atom to a B plane atom. We have also seen that in a finite film of $2n + 1$ occupied atomic planes the outer plane will be A or B depending on whether n is odd or even (where the central plane is defined to be an A plane) and that if $\overline{X}_3^{\pm}$ surface states exist for an A surface plane then $\overline{X}_1^{\pm}$ surface states

exist for a B surface plane. We now see that an interplanar shift of the outermost peak of the surface wave function by a change of crystal potential has the same effect on its symmetry as removing one plane of atoms from the surface. One can also see from energy considerations why the symmetry of the surface wave function changes. At the outermost B plane the previous and Cambridge wave functions are very small, whereas the pure overlap wave function is very large. It is able to avoid the repulsive pseudopotential at the outermost B plane atomic sites by having $\bar{X}_1$ symmetry because of the $\bar{r} = (\frac{1}{2}, \frac{1}{2})$ nodal line for $\bar{X}_1$ states. Exactly the same reasons account for the changed symmetry of the $\bar{M}$ surface states.

We also note from Fig. 2 that the lower $\bar{X}$ surface state wave functions are almost identical for our previous potential and for the Cambridge potential. For $\bar{r}$'s different from $\bar{r} = (\frac{1}{2}, \frac{1}{2})$ shown in the figure, the differences are greater but still not appreciable. This is because the outermost peak of the wave functions occur in a region where the potentials are almost identical. These surface states are too low in energy to peak outside the jellium edge. Therefore the difference in these two potentials does not have much effect on the wave functions. The surface states in the upper $\bar{X}$ gap peak just inside the jellium edge and it is there that we see the largest effects of the difference in potentials. Figure 3 shows $\bar{X}_1^+$ surface states from the upper gap, plotted for two different $\bar{r}$ points. We see that the Cambridge potential causes the wave function to fall off more

FIG. 2. Surface states from the lower $\bar{X}$ gap for each of the three potentials. $\bar{r} = (0, 0)$ for $\bar{X}_1^+$ and $\bar{r} = (\frac{1}{2}, \frac{1}{2})$ for $\bar{X}_3^+$.

rapidly outside the jellium edge. To tie on smoothly to this decay, the portion of the wave function which is inside the jellium edge must peak a little further back from the edge. This is coupled with a shift in eigenvalue from -0.21 Ry for the previous potential to -0.17 Ry for the Cambridge potential. This difference in peak position and eigenvalue is not matched by any constant change in peak height or decay constant inside the jellium edge. In fact we see the Cambridge peak is the larger of the two at $\bar{r} = (0, \frac{1}{2})$, while the reverse is true at $\bar{r} = (0, 0)$.

Our first conclusion from the above is that the differences between our calculation and Boudreaux's cannot be explained by the differences
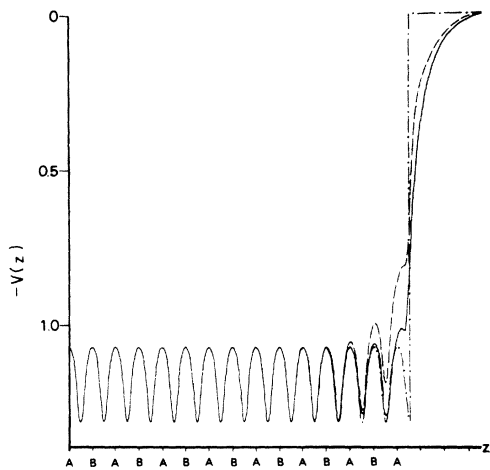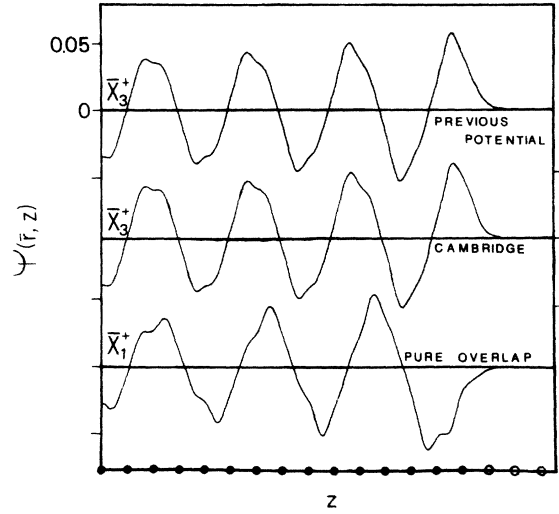

FIG. 1. $\bar{G} = (0, 0)$ Fourier transforms of the three potentials used in this study. The solid line shows our previous potential; the dashed line shows the pure overlap potential; the line of dots and dashes shows the Cambridge potential. Occupied layers are labeled as A or B type.
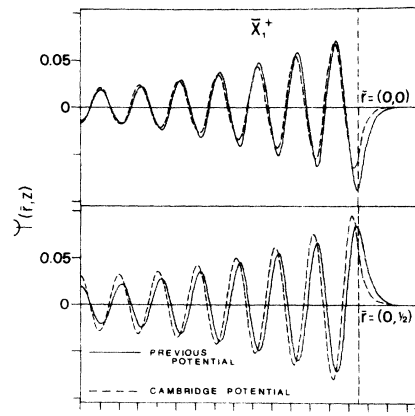

FIG. 3. $\bar{X}_1^+$ surface state from the upper $\bar{X}$ gap. Results for our previous potential and the Cambridge potential are compared. The jellium edge is shown by the vertical dashed line.

between the potentials. (Perhaps the largest difference in our results is for (110) aluminum where Boudreaux found no surface states whereas we found surface states in every two dimensional energy band gap.) There are of course other differences in the calculations. We considered a film sufficiently thin that the surface states are still rather appreciable even at the center of the film whereas Boudreaux considered a semi-infinite crystal. While this will shift the energy of the surface states, it cannot cause their disappearance. Boudreaux used only two Fourier components, V_{111} and V_{200}, in his pseudopotential but all the energy gaps (below the vacuum energy) in which the surface states occur are due to degenerate plane wave states split by V_{111} or V_{200} and therefore the higher $V_{\vec{K}}$ should not have an appreciable effect on the surface states. Finally, although our mathematical methods of calculation are entirely different, they must yield the same result when carried to convergence except for those small differences we have discussed due to the difference in potential. We therefore are forced to conclude that there must be some error in Boudreaux's calculation.

Our second conclusion is that at least for low-lying surface states the most important part of the potential is its behavior inside the jellium edge. It is those surface states which lie close to the Fermi surface which play a major role in chemisorption and catalysis. If the work function is large these states will be low enough in energy to peak well inside the jellium edge. It is therefore the behavior of the potential over the last few occupied layers which must be correct if the surface states are to be found accurately enough to determine their role in chemisorption and catalysis. It has previously been assumed that the discontinuous termination of the Cambridge potential is its most unphysical attribute. But our results cast doubt on the procedure of using a bulk potential up to the jellium edge. For the case of aluminum this worked well because the actual potential rises only slightly over the last few layers and the integrated difference between the Cambridge and actual potentials weighted by the square of the surface wave function is very small. On the other hand in larger-r_s metals such as lithium[8] the potential drops below the bulk potential over the last layer or so. In ionic and covalent materials the surface double layer is known to cause band bending and in that case the Cambridge potential is expected to be especially poor.

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