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James R. Chelikowsky, M. Schlüter, Steven G. Louie,
and Marvin L. Cohen

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Self-Consistent Pseudopotential Calculation for the (111) Surface of Aluminum*

James R. Chelikowsky, M. Schlüter,†
Steven G. Louie‡ and Marvin L. Cohen
Department of Physics, University of California
and
Inorganic Materials Research Division,
Lawrence Berkeley Laboratory, Berkeley, California 94720

Abstract

The electronic structure of the (111) surface of aluminum is calculated using self-consistent pseudopotentials. Surface states are identified and the (111) work function calculated. The behavior of the total charge density and potential near the surface is displayed and discussed. Self-consistency is found to be of crucial importance.

We have calculated, using self-consistent pseupotentials, the electronic structure for a (111) surface of aluminum. In agreement with calculations by Caruthers, Kleinman and Alldredge,[1] but in contrast with Boudreaux,[2] we identify surface states below the fermi level, E_F, at both Γ and K in the two dimensional Brillouin zone. The charge density profile is presented for the most localized surface state, which occurs at K, and for the total charge density. The behavior of our resulting self-consistent potential is also

displayed as a function of distance into the bulk. A comparison of this potential with the results of other techniques for obtaining a "realistic" surface potential for aluminum emphasizes the requirement of a self-consistent calculation. We also calculate a work function for the (111) surface which is in a satisfactory accord with experiment.

While self-consistent calculations exist for simple models, e.g. jellium,[3] and have recently been performed for sodium[4] and lithium,[5] as yet, no self-consistent calculations have been performed on polyvalent metals such as aluminum. This is unfortunate because in the previous cases surface states are not found below E_F and, therefore, cannot contribute to the self-consistency process. Surface states are not, of course, observed in jellium because they are specifically excluded by the free electron nature of the band structure, while in monovalent metals, which possess no band gaps below the fermi level,[6] the observed states lie above E_F. There is also the open question of conflicting calculations between Boudreaux, and Caruthers, Kleinman and Alldredge (CKA). Boudreaux used a step function potential for the transition between the bulk potential and the vacuum, while in the CKA calculation an aluminum bulk potential was merged smoothly into a jellium potential[3] at some arbitrary point near the surface. Neither calculation was performed in a self-consistent fashion. Boudreaux found surface states for the

(111) surface to exist only at Γ; however, CKA found surface states at Γ, K and M. In order to account for these varying results CKA examined the effect of the two different potentials on the surface properties. They concluded that the differing potentials could not reconcile their calculation with that of Boudreaux and suggested an error had been made in his calculation. However, CKA noted in the course of their study that the behavior in the transition region between vacuum and bulk was crucial in determining an accurate picture of the surface states, thus casting some doubt on the appropriateness of the matching scheme of jellium to bulk potentials. A self-consistent calculation, not suffering from such a defect is consequently of prime importance for an understanding of the surface of Al.

The method which we have employed in this calculation has been discussed elsewhere[7,8] and thus will only briefly be outlined below. The crucial point is that we periodically repeat a slab of aluminum with a (111) surface exposed to vacuum on both sides. In this sense, we retain a periodic system and, hence, the usual techniques of the pseudopotential method may be applied. Specifically, we have taken a twelve layer Al slab with a vacuum region of three interlayer distances for each surface over which the wavefunctions of the slab are allowed to decay. Thus, the method is somewhat similar to the technique of Alldredge and Kleinman[9] with the principle difference being that they have the additional requirement that each plane wave component of the wavefunction

must vanish at the midpoint of the vacuum region between neighboring slabs. Thus our method allows the potential in the surface region to determine the decay of the wavefunctions into vacuum without this additional, and physically unnecessary constraint.

Although we do not have a semi-infinite crystal, the experience of Alldredge and Kleinman[5] suggests very accurate results may be obtained from thin films with reference to the semi-infinite case. The main problems which may arise from the use of thin films are a) an interaction of surface states on opposite sides of the film may lift a degeneracy which would occur if the film were infinitely thick, and b) the surface state wavefunctions decay so slowly into the slab that the film's thickness does not permit such states to be distinguishable from bulk states. However, for a dozen or more layers these are not insurmountable problems.

As in our previous work[7,8] we use a Heine-Animalu core potential[10] which is then screened in a self-consistent manner using the pseudocharge density.[11] A Hartree potential is derived from this charge density via Poisson's equation, and an exchange potential of the Slater type added.[7,8] Because the bare Al^{3+} ion potential diverges as $1/q^2$ for small wavevector q, the usual iteration procedure to obtain self-consistency is not practical.[5] However, the screening potential may be altered in a systematic fashion until the "input" screening potential and the "output" screening potential are in essential

agreement. In this manner we were able to achieve agreement to within one percent for the input and output potentials. For this accuracy the eigenvalues are stable to better than 0.02 Ry.

To determine the required screening potential an accurate fermi level must be calculated. This was accomplished by calculating the eigenvalues and eigenvectors over a grid of 294 points in the two dimensional brillouin zone. The calculated value for E_F was 0.85 Ry above the conduction band minimum in good accord with the bulk value of 0.86 Ry.

We emphasize again the importance of self-consistency. If the total pseudopotential is taken as a superposition of linearly screened atomic pseudopotentials a negative work function will result.[1] This can be remedied by a superposition of atomic pseudopotentials which are constructed by extrapolating a smooth curve through points determined empirically from the bulk so that a proper work function results. However, this practice is deficient in two respects. First, the rise of the resulting potential from bulk to vacuum is unphysically abrupt and second, this procedure does not incorporate any response to the Friedel oscillations which are known to occur in the screening potential.[3] In Fig. 1 we indicate our resulting self-consistent potential averaged parallel to the surface and plotted as a function of distance into the slab. We note that over the last few layers this potential actually drops below the bulk potential by approximately 0.1 Ry. This is a result of the self-

consistency process and does not occur for a superposition of atomic pseudopotentials. It has also been observed in the case of Li,[5] and it casts doubt on the CKA procedure of matching jellium to bulk potentials.

Once the fermi level has been determined the work function, ϕ, can be evaluated from

$$\phi = v(\infty) - E_F ,$$

as indicated in Fig. 1. The value for $v(\infty)$ is assumed in our calculation to be negligibly different from the value of the potential at the midpoint of the vacuum region between adjoining slabs. The calculated value is 0.38 Ry, which unfortunately cannot be compared directly to the experimental value of 0.31 Ry available for polycrystalline Al.[12] In any event such a comparison is not of great value in judging the accuracy of a surface calculation as a uniform shift in the potential at large distances would alter ϕ, but not the resulting surface states. Considering the uncertainty involved with the polycrystalline value,[13] we consider the agreement as adequate.

In Fig. 1 we display our total charge density in the (110) plane, along with the averaged charge density again plotted as a function of distance into the bulk. The calculated charge density is significantly perturbed from the bulk charge only outside the second surface layer of the aluminum ions. The charge deeper into the bulk is in good accord with the bulk density.[14] Although we use this

pseudocharge density to screen the ions, the actual charge density should yield similar results except within the core regions and, thus, should provide an accurate screening potential. The averaged charge density, as in the jellium case,[3] exhibits the usual Friedel oscillations in the total charge near the surface. The maximum oscillation indicates a fluctuation of about 5% above the bulk; this is larger than in jellium for the equivalent density,[3] and in accord with the trend observed in Li.[5]

To determine the existence of surface states we have examined the charge density for all eigenvalues below E_F at high symmetry points in the two dimensional zone. In this context we make use of the projected bulk band structure provided by the CKA calculation. It is, of course, within the "projected gaps" that bona fide surface states may exist.[1,6] In particular, we are interested in those states below E_F which could be experimentally detected. Preliminary attempts to detect such states have, in fact, been carried out through photoemission experiments on polycrystalline films.[15] The results indicate that the bulk density of states of Al is indeed altered by the presence of surface states. In the bulk, the density of states exhibits peaks at 0.29, 0.18 and 0.05 Ry below the fermi level; the photoemission results suggest a "filling-in" between the peaks due to the occurrence of surface states.

Our results indicate the existence of surface states below E_F at Γ and at K,[16] as mentioned, in agreement with the

results of the CKA calculation, but not with that of Boudreaux. At Γ the surface state occurs at 0.33 Ry below E_F and at K we have two surface states at 0.15 Ry and 0.07 Ry below E_F. These latter states do indeed occur between the bulk density of states peaks, and could account, in part, for the photoemission results. The most localized surface state is the upper state at K at 0.07 Ry. In Fig. 2 we display the averaged charge (as in Fig. 1) and a contour plot for the charge in the (110) plane. This state occurs in a rather large energy gap in the projected band structure and its decay is more rapid than the other state at K at 0.15 Ry or the surface state at Γ. From the contour plot we see that the charge density of this state is localized in a "cavity" near the surface formed by the first and second atomic layers. Since this state occurs quite near E_F and is localized very strongly near the surface, it is expected to be chemically active.[1] The 0.15 Ry surface state at K is not as localized, and is quite sensitive to the surface potential. As with the 0.07 Ry state at K it has charge localized in the cavity regions, but peaks further from the surface. Finally, the surface state at Γ, which occurs in the bulk band gap at L in the three dimensional zone, decays quite slowly falling only by 10% from the peak value at the surface to the mid-point of the slab.

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Figure Captions

Figure 1. The top figure indicates the self-consistent potential averaged parallel to the surface and plotted as a function of distance into the bulk. The middle figure shows a similarly averaged total charge density (normalized to one electron per unit cell, Ω cell = 300 $\mathring{A}^3$). The bottom figure shows the total charge density in the (110) plane, with the same normalization; the contour spacing is in units 0.15. Only the minima of the charge density are labelled. The ionic positions are indicated by the black dots.

Figure 2. The top figure shows the averaged charge as in Fig. 1 for the surface state at K. The bottom figure shows the charge density for this state in the (110) plane. The contours are spaced by units of 0.75.

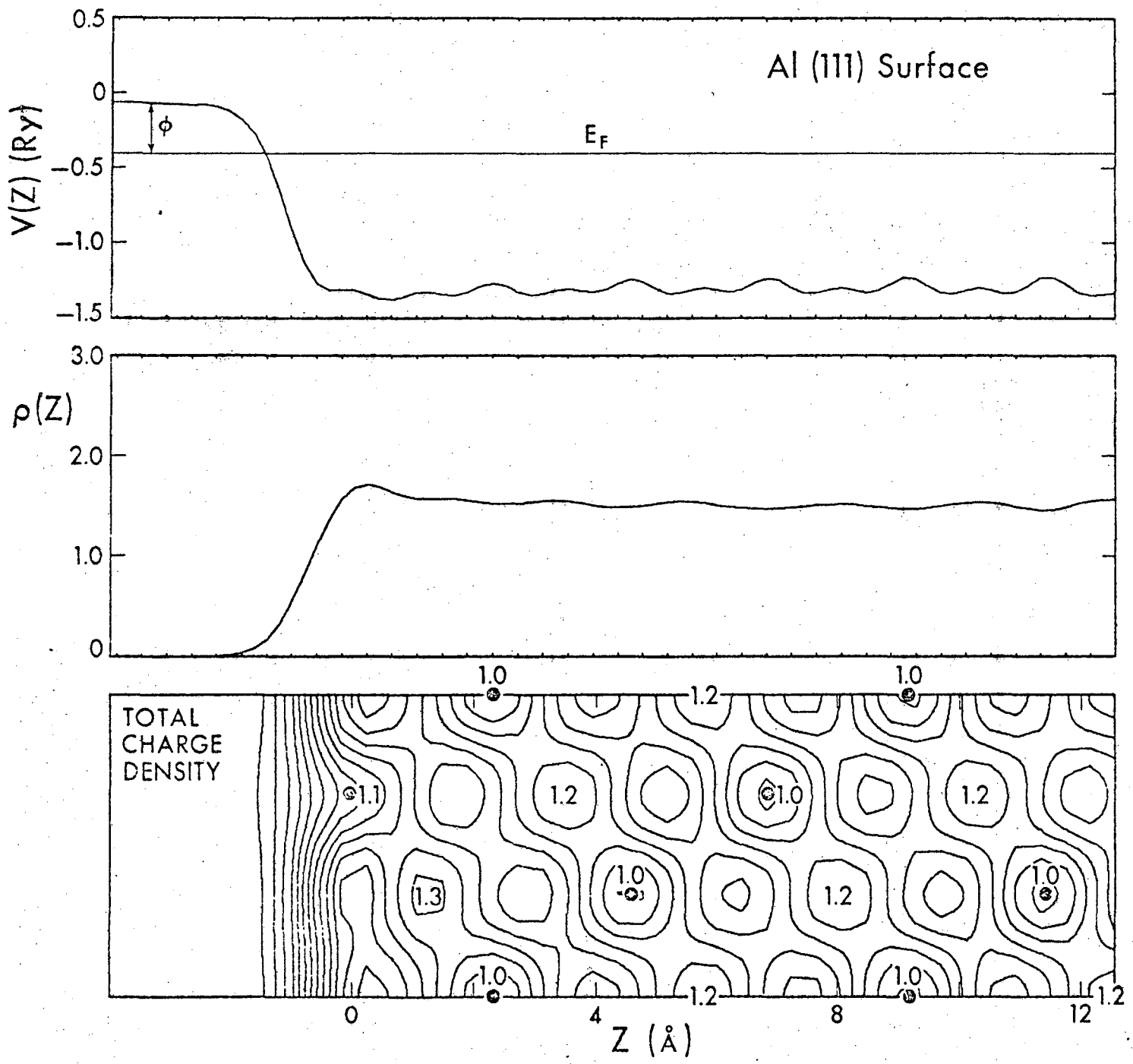

Fig. 1

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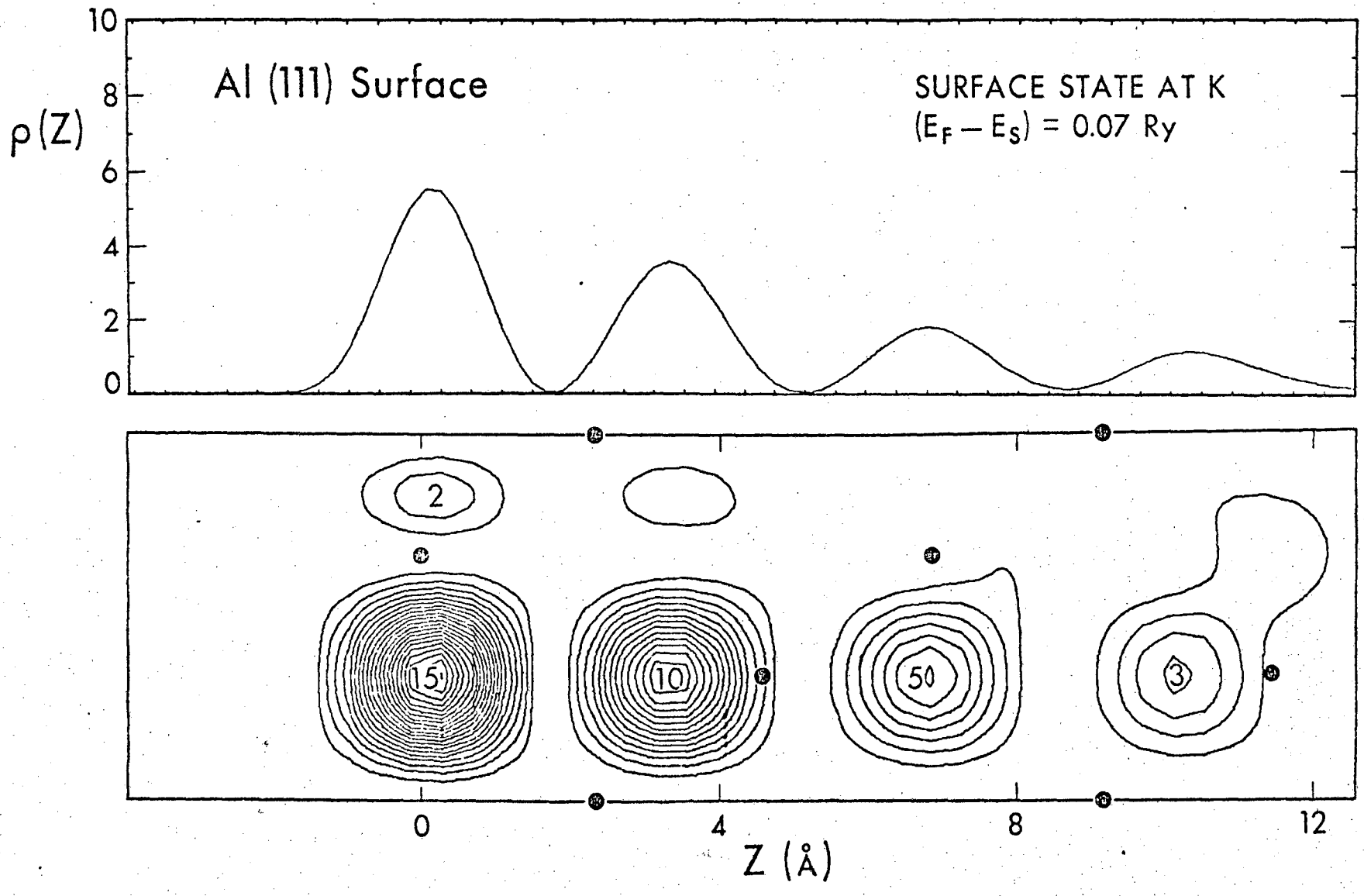
Al (111) Surface
SURFACE STATE AT K
$(E_F - E_S) = 0.07$ Ry
ρ(Z)
10
8
6
4
2
0
2
15
10
50
3
0
4
8
12
Z (Å)

Fig. 2

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