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Surface Relaxation Influenced by Surface States

Vasile Chis and Bo Hellsing

*Solid State Physics, Experimental Physics, Göteborg University and Chalmers University of Technology,
S-412 96 Göteborg, Sweden*
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A detailed theoretical investigation of the relaxation of the simple metal surface Al(100) is presented. We show the influence of electronic surface states in this context. The sign and magnitude of the relaxation of the topmost atomic layers is mainly determined by the rearrangements of the surface state charge. The degree of surface relaxation convergence, with respect to the number of slab layers, is determined by the location of the surface state band relative to bulk bands.

When a solid is cut, the atoms near the surface are exposed to different forces from those in the bulk of the material. The atoms near the newly created surface tend to relax mostly perpendicular to the surface to minimize the total energy. A proper description of the ionic forces is crucial to obtain the relaxed atomic structure. The final surface atomic positions will determine the surface electron structure properties such as, e.g., work function and surface energy and also the surface lattice dynamics. We show that electronic surface states could play a crucial role. Although in general, only the uppermost two or three atomic layers will show any appreciable relaxation, an order of magnitude larger number of layers might be required in a slab calculation due to deeply penetrating surface states.

The relaxation and dynamical properties of the Al(100) surface has been the objective of several investigations based on different theoretical methods. Already more than a decade ago, Bohnen *et al.* [1] showed that slight variations of the force constants in the surface significantly influence surface phonon frequencies near Brillouin zone boundaries. The Al(100) surface has an occupied electronic surface state band and we have found a clear correspondence between the relaxation and the surface state.

Experimental investigations by Davis *et al.* [2] of the relaxation of the interlayer spacing between the two top atomic layers, Δd_{12}, of Al(100) yields an expansion of 1.8%. Semiempirical calculations yield an *inward* relaxation -2.7% (embedded atom method) [3] and -3.0% (effective medium theory) [4], while *first-principles* studies by Bohnen *et al.* [1] and Zheng *et al.* [5] suggest an *outward* relaxation (expansion) by 1.2% and 1.8%, respectively. The semiempirical methods obviously do not describe the surface ionic forces correctly. Both of the *first-principles* calculations yield correct outward relaxation. However, due to the deeply penetrating electronic surface state, far too few slab layers have been used in order to grasp the ground state relaxed atomic structure. This is illustrated by our calculated Δd_{12} shown in Fig. 1 in comparison with the experimental result.

Based on simple arguments, one would expect that for a nonmetallic surface, the relaxation would be inward simply due to breaking of local bonds, while for a metallic surface the relaxation could be outward as the top layer tries to adjust to the displaced valence electron density. However, it has been shown [5] that for a simple metal such as aluminum, both inward, Al(110), and outward, Al(100), relaxation take place.

Al(100) exhibits, as many other single crystal metal surfaces [6], a surface localized electronic band. In the case of Al(100) the binding energy of the surface state is about 3 eV in the $\bar{\Gamma}$ point and thus these band states will be partly occupied. Our detailed investigations, resolving the redistribution of valence electron charge in the relaxation process of the uppermost surface layers, show that the surface state electrons play a dominant role. As a consequence, we notice that in a slab calculation the convergence of the surface layer relaxation, as function of number of slab layers (N), is determined by the location of the surface state band relative to the bulk bands. For Al(100), the surface state band is close to the lower edge
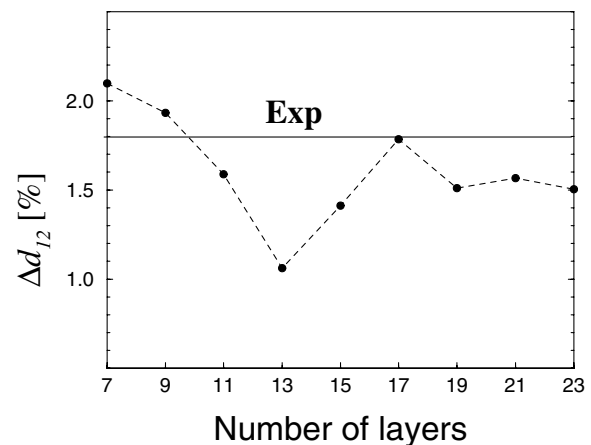

FIG. 1. Interlayer relaxation Δd_{12}. Filled circles are calculated results and the dashed line serves as a guide for the eye. The horizontal solid line marks the experimental value (Ref. [2]).

of the projected bulk band gap and thus its wave functions penetrate far into the bulk. Thus a large number of slab layers are needed to avoid interference effects between the two slab surfaces. To our knowledge, no previous theoretical investigations have been presented where the role of surface states have been pointed out as crucial for the understanding of the surface relaxation.

The calculations were based on *first-principles* density functional theory (DFT) with the local density approximation (LDA) for the exchange and correlation potential. The electron wave functions were expanded in plane waves with an energy cutoff of 12 Ry and the Al ion pseudopotential described by norm-conserving pseudopotentials. Calculations are performed for slabs with $N = 7\text{--}23$ and six layers of vacuum. The supercell is defined by $(L_x, L_y, L_z) = (b, b, L)$, with $b = a/\sqrt{2} = 5.3033$ a.u, where a is the conventional lattice parameter of Al and L is determined by N. The Brillouin zone was sampled at k points according to the Monkhorst-Pack $16 \times 16 \times 1$ mesh. To improve the convergence, a finite temperature smearing of $k_B T = 0.7$ eV was included. The relaxation of the system is performed according to the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm. The Hellman-Feynman forces acting on each atomic layer perpendicular to the surface were calculated and the structure was relaxed in the z direction until these forces were less than 2.6 meV/Å. The surface projected band structure of the relaxed surfaces was determined by calculating the Kohn-Sham eigenvalues in 81 k points along the symmetry lines $\bar{X}\text{-}\bar{\Gamma}\text{-}\bar{M}$ in the surface Brillouin zone (SBZ).

The calculation of the x, y-averaged valence electron density, $\bar{\rho}(z)$, has been done in two ways: one, by averaging $\rho(\vec{x}, z)$ over the planar points, $\vec{x}$, in the x, y plane of the supercell (Fig. 4). Second, by applying a well motivated free-electron approximation in the x, y plane with band masses determined by the self-consistent bands near the $\bar{\Gamma}$ point (Fig. 6). We sum the integrated parts of the occupied bands over the SBZ to get the density. Thus we can decompose the valence electron density in parts originating from surface and bulk states.

We present part of the band structure for the 13 layer and 23 layer slab in Fig. 2 in the reduced zone scheme. The interaction of the two slab surfaces is reflected in the splitting of the odd and even symmetry surface state band (dashed lines in Fig. 2). An increase of N will reduce the gap ΔE between the surface states. ΔE versus N is calculated for 7–23 layers slabs and is well approximated by an exponential function, $\Delta E = E_0 e^{-\alpha N}$, where $E_0 = 3.235$ eV, $\alpha = 0.132$. The energy gap for the 13 and 39 layer slab is found to be 580 meV and 19 meV, respectively. This compares well with calculations by Caruthers *et al.* [7], 570 meV and 27 meV, respectively. According to this analysis, $N > 41$ is required in order to obtain $\Delta E < 10$ meV for Al(100), which is optimal to obtain an accuracy compatible with the typical resolution of a DFT
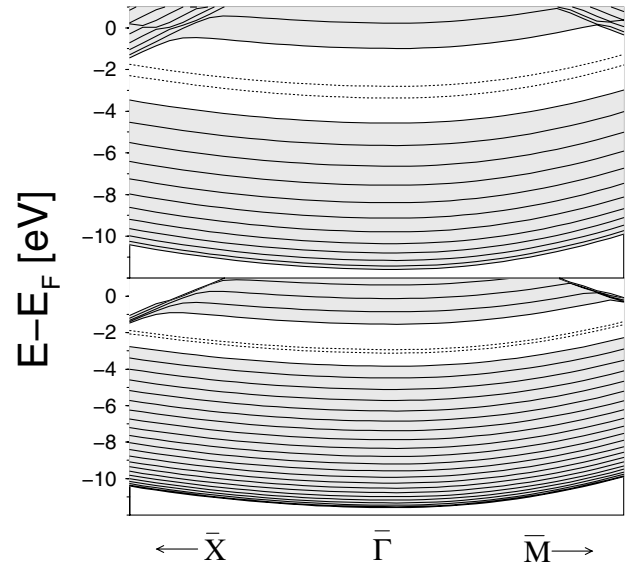

FIG. 2. Energy bands of Al(100) for the slabs of 13-layer (top) and 23-layer (bottom). The gray area represents bulk bands areas and the dashed lines the surface states.

calculation and, e.g., high resolution photoemission spectroscopy data. The bulk band gap reduction with N shown in Fig. 2 does not have a large effect on the surface density variation with N (shown later) and thus not on the surface relaxation. However, the reduced energy separation between the surface bands and the lower bulk band edge with N will increase the decay length of the surface state (approximately inversely proportional). Fortunately, this increase is slower than the increase of the slab thickness with N. This phenomena is most likely partly responsible for the apparent convergence previously reported [5] up to $N = 9$.

The relaxation of the top layers of a slab is determined by the forces on the ions set up by the redistribution of valence electron charge density taking place as soon as the surface is created. Within the Born-Oppenheimer approximation, the electron density adjust instantaneously to a change in the ionic lattice structure, determined by the direction of the net ionic forces. As the net ionic forces eventually vanish, the relaxed lattice structure is obtained. This scenario can be mapped in detail in the calculations.

The initial ionic forces perpendicular to the surface prior to the actual ionic relaxation is determined by the self-consistent electron density for the truncated bulk lattice structure. In Fig. 3 we show these net forces acting on the first and second layer as a function of N.

We note that independent of N, the initial force acting on the first layer is outward, while slightly inward on the second layer. Thus we expect that these two layers will start to move apart as the ions start to respond to the forces. Furthermore, the result for the $N = 13$ indicates a minimum of this tendency, which is consistent with the dip in Δd_{12} shown in Fig. 1. The variation of the force
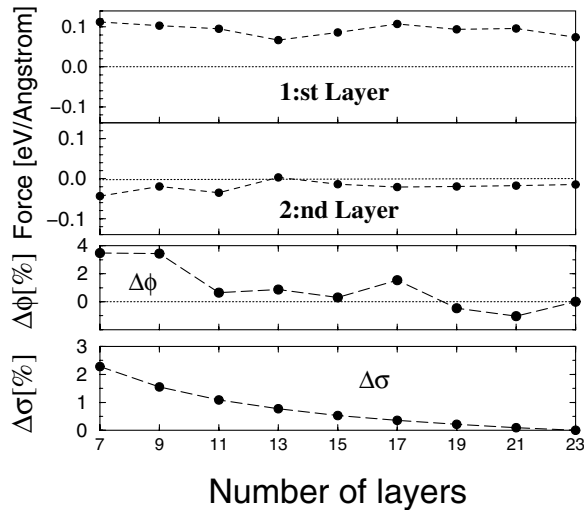
FIG. 3.   Top: Initial forces (see text) acting on the first and second layer. Positive and negative values indicate direction towards vacuum and slab center, respectively. Middle: Work function change; $\Delta\Phi(N) = [\Phi(N) - \Phi(23)]/\Phi(23)$. Bottom: Surface energy change; $\Delta\sigma(N) = [\sigma(N)/N - \sigma(23)/23]/\sigma(23)/23$.

with N in the region 7–23 layers indicates the slow convergence. As the force is determined by the electron density, the major changes in the electron density take place near the topmost layer. To get further insight, we have analyzed the electron density in more detail.

In Fig. 4 we compare the total valence electron density for the unrelaxed and relaxed lattice structure. We note the general trend that the relaxation drives the near-surface electron density towards the vacuum region. However, the magnitude of this tendency depends on N.

Comparing the 13 and 23 layer slabs, we observe a consistent trend when comparing the force in Fig. 3, valence electron density in Fig. 4, and finally Δd_{12} in Fig. 1.

We now show that this layer dependence brings about the evidence for the importance of the surface states in the relaxation process.

To see this, we integrated the surface electron charge, from the position of the unrelaxed second layer to a position far into the vacuum, for both the unrelaxed and the relaxed lattice. The percentage difference is shown in Fig. 5 and shows a similar structure as the layer dependence of Δd_{12} shown in Fig. 1.

To illustrate the connection between the relaxation and the surface states, we resolve the relaxed electron density of the 13 and 23 layer slabs in terms of contributions from bulk and surface states, respectively (Fig. 6).

It is obvious from Fig. 6 that what makes the difference in electron density at and outside the uppermost lattice plane is the charge carried by surface state bands. In this region, the contribution from bulk states is essentially the same for the 13 and 23 layer slab (as well as for the rest of the investigated slabs).

For very thick slabs ($N \rightarrow \infty$) the odd and even surface state wave functions, with respect to the slab center, become equal in the surface region where they have any appreciable amplitude and if x, y-averaged, their nodes will coincide with the lattice planes. However, for a slab thickness less than twice the surface state wave function decay length, the odd and even wave functions will be shifted relative to each other in the region of the surface and their nodes will not coincide with the lattice planes; thus the charge density in the surface region will vary with N and accordingly the ionic forces and therefore the lattice relaxation.

We thus have the following scenario. As the surface is created, the valence electrons relax rapidly. The forces built up drive the top ionic layer outwards. During this process, the electron density will be pushed even further. The further the electron density is pushed outwards the further the top layer will be displaced. The electron charge density from bulk band states will not change
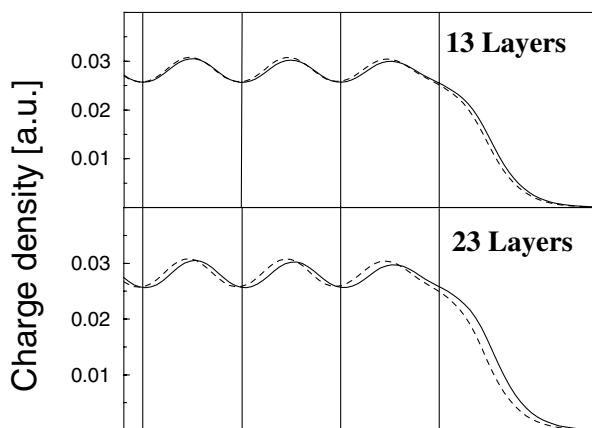

FIG. 4.   Valence electron density, for a 13 and 23 layer slab. The dashed and solid lines represent the unrelaxed and relaxed geometry, respectively. The vertical lines represent the ion core positions of the unrelaxed uppermost four layers.
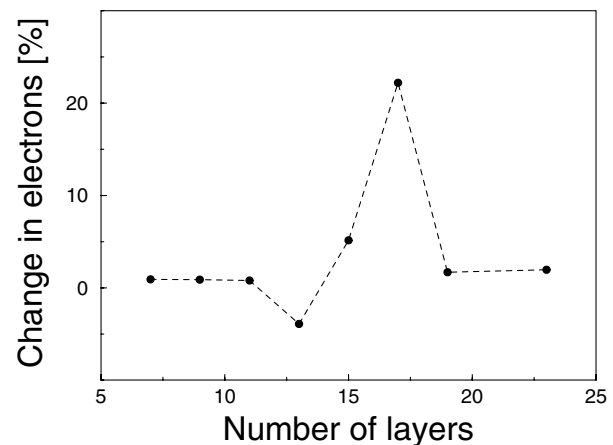

FIG. 5.   Percentage change of valence electron charge due to the relaxation in the region from the unrelaxed second layer out into the vacuum.
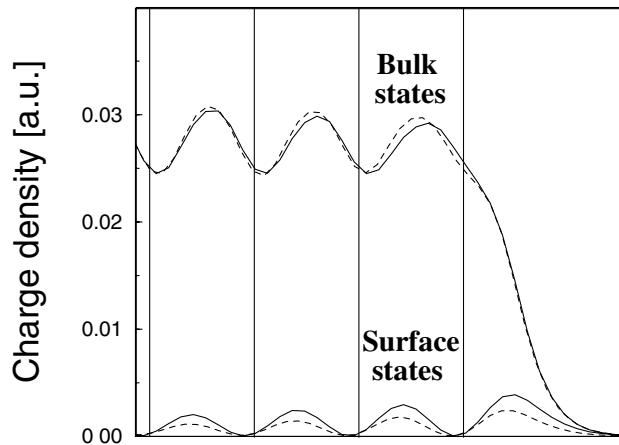
FIG. 6. Valence electron density for a 13 (dashed line) and 23 layer slab (solid line). Contributions from bulk and surface states indicated. The vertical lines represent the ion core positions of the unrelaxed uppermost four layers.

appreciably with N in the focused region, while the density from the surface states is responsible for most of the electron density variation. The surface energy and work function variations with respect to N are shown in Fig. 3. The surface energies converge smoothly while the work function shows a similar variation as the top layer forces and relaxation. This is understandable as the surface energy is an integrated quantity based on total energies while the work function is really determined by the dipole generated by the relaxed surface electron density. For the surface Al(111), we expect the same mechanism to be responsible for the observed outward relaxation, as the observed surface band electron structure is similar [3].

In Table I, some of our results for the relaxation are shown together with results of previous calculations and experimental data. Our calculated value for Δd_{12}, 1.93% for the nine layer slab, agrees well with the result 1.89% in a previous *first-principles* calculation by Zeng *et al.* [5]. By chance the nine layer results happen to agree well with the experimental result (1.84%). However, our study shows that Δd_{12} is far from convergence for a nine layer slab. The 23 layer result for Δd_{12}, 1.50%, is more close to a converged value. We find a value about 20% smaller than experiment. This underestimate of Δd_{12} is not surprising as LDA is well known to give an over-binding. The semi-empirical results [3], $\Delta d_{12} = -2.7\%$, which are based on fitting to elastic bulk properties, indicate the importance of including the surface electron structure.

In conclusion, we have shown that the relaxation of the Al(100) is strongly influenced by the surface state bands. The slow convergence of the relaxation, in particularly for the uppermost layer, is a clear signal of a deeply penetrating occupied surface state band. We have estimated that for Al(100), an optimal result for the relaxa-

TABLE I. Surface relaxation of Al(100) as function of number of slab layers (L). (∗) denotes results of this work.

	Δd_{12}	Δd_{23}	Δd_{34}	Δd_{45}	Ref.
9L	1.93	1.40	0.87	1.06	(∗)
15L	1.41	1.13	0.83	0.60	(∗)
23L	1.50	1.19	0.64	0.66	(∗)
Theory (9L)	1.89	4.12	2.96	2.94	[5]
Theory (15L)	1.2	0.2	−0.1	⋯	[1]
Theory	−2.7	−0.1	⋯	⋯	[3]
Experiment	1.84	2.04	⋯	⋯	[8]

tion of a *first-principles* study with a typical accuracy of 10 meV, which also is about the present resolution in HRPES experiments, requires at least a 41 layer slab. In general, the closer an occupied s, p surface state band appears relative to the bulk bands the greater the decay length of the surface states and thus the greater the number of slab layers is required to avoid interacting surface states. A proper surface relaxation is important for a realistic description of (i) the surface electron structure, e.g., the work function and surface energy, and (ii) surface ionic forces that will determine the surface dynamics. Finally we propose more extensive slab calculations of surfaces with an experimentally determined surface band structure similar to Al(100). Photoemmision data indicate that, e.g., Ag(111) and Mg(0001) have a partly occupied s, p surface state band slightly above the lower bulk band edge, and thus they serve as good candidates.

[1] K.-P. Bohnen and K.-M. Ho, Surf. Sci. **207,** 105 (1988).
[2] H. L. Davis, J. B. Hannon, K. B. Ray, and E. W. Plummer, Phys. Rev. Lett. **68,** 2632 (1992).
[3] E. V. Chulkov and I. Yu. Sklyadneva, Surf. Sci. **331,** 1414 (1995).
[4] P. D. Levsen and J. K. Norskov, Surf. Sci. **254,** 261 (1991).
[5] J.-C. Zheng, H.-Q. Wang, C. H. A. Huan, and A. T. S. Wee, J. Electron Spectrosc. Relat. Phenom. **114,** 501 (2001).
[6] E. V. Chulkov, V. M. Silkin, and P. M. Echenique, Surf. Sci. **437,** 330 (1999).
[7] E. Caruthers, L. Kleinman, and G. P. Alldredge, Phys. Rev. B **8,** 4570 (1973).
[8] W. Berndt, D. Weick, C. Stampfl, A. M. Bradshaw, and M. Scheffler, Surf. Sci. **330,** 182 (1995).
[9] S. Baroni, A. Dal Corso, S. de Gironcoli, and P. Giannozzi, Plane-Wave Self-Consistent Field, http://www.pwscf.org.