

## Deep multilayer relaxations on the Al(001) surface: *Ab initio* all-electron calculations

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The multilayer relaxations of pure Al(001) surface were theoretically analyzed using *ab initio* all-electron calculations. Big slabs (23 atomic layers+20 vacuum layers) were needed to capture the deep pattern of multilayer relaxations. We have obtained an outward relaxation for the surface interlayer distance and deep interlayer relaxations characterized by a damped oscillation wave pattern, with several interlayers by cycle. The first three interlayers were found to be expanded, while the following four interlayers were found to be contracted. A charge density analysis allows us to correlate the outward relaxation with the population imbalance between the atomiclike  $p_{\parallel}$  and  $p_{\perp}$  orbitals of atoms at the surface. Multilayer relaxations are related to the presence of distributed Friedel oscillations in the charge density difference between bulk and bulk-truncated slabs. Work function and surface energy results are also presented and discussed. In order to calculate the latter, a high precision Al bulk energy value was obtained irrespective of whether it is calculated from the fcc symmetry or slab derived when the same method-dependent parameters as well as big slabs are used. Error bars, as a measure of the theoretical precision, are included for all studied properties. Our results agree with the available experimental measurements and, partially, with other theoretical calculations. Previous experimental work on this surface has never considered the possibility of such deep relaxations. Our results should motivate further experimental research on the multilayer relaxations of the Al(001) surface.

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### I. INTRODUCTION

When a surface of a crystal is formed, the surface atomic layer and (very often) several atomic layers below present relaxation and (or) reconstruction. The presence of relaxation and (or) reconstruction depends on the particular material of interest. While semiconductor surfaces show a variety of patterns of reconstructions, metallic surfaces usually only relax the atomic positions in the direction perpendicular to the surface, maintaining the crystal symmetry parallel to the surface.<sup>1</sup> For open low-index metallic surfaces, these relaxations are usually experimentally found to be inward, whereas they can be inward or outward for closed-packed low-index metallic surfaces, depending on the material.<sup>2</sup> For even more open, high-index metallic surfaces, the experimental evidence exhibits only inward relaxation.<sup>3</sup> The description of a surface either as inward relaxed (or contracted) or as outward relaxed (or expanded) means, in this context, that the interlayer spacing between the outermost two atomic layers (also referred to as the surface interlayer or first interlayer) is contracted or expanded, respectively, with respect to the bulk interlayer spacing. We refer to a system as having multilayer relaxations when deeper interlayer distances are also modified with respect to the bulk. It is well accepted today that multilayer relaxations are present for many metallic surfaces, even if it is not easy to measure them experimentally because they might be rather small. For a particular set of  $i$  and  $i+1$  neighboring layers, the relaxation  $\Delta d_{i,i+1}$  (in percent) of the corresponding interlayer distance  $d_{i,i+1}$  is defined by

$$\Delta d_{i,i+1} = \frac{d_{i,i+1}(\text{relaxed}) - d_{i,i+1}(\text{bulk})}{d_{i,i+1}(\text{bulk})} 100, \quad (1)$$

where a positive (negative) sign indicates an expansion (contraction).

On the other hand, to characterize how open a given surface is, one usually defines the *surface packing fraction* coefficient or *compactness* of the surface as the ratio between the surface spanned by bulk touching spheres inside the surface unit cell and the surface spanned by the surface unit cell itself. For fcc Al the compactness is 0.55, 0.78, and 0.91 for the (110), (001), and (111) surfaces, respectively, with the (110) surface being the most open and the (111) the most closed-packed of the three surfaces considered. The intermediate compactness of the Al(001) surface makes it an interesting case to study. The topmost interlayer distance for the Al(110) surface is found to relax inward (experimentally ranging from  $-6.9\%$  to  $-11.2\%$  see Table VII of Ref. 4 and references therein), whereas the Al(111) surface relaxes outward (experimentally ranging from  $+0.9\%$  to  $+2.2\%$  see Table III of Ref. 5 and references therein). Moreover, Al(110) and, to a lesser extent, Al(111) surfaces both exhibit experimentally detectable multilayer relaxations (see the above mentioned references). Since the compactness of the Al(001) surface is in between the Al(110) and Al(111) surfaces, one may raise the question whether the Al(001) surface will relax inward or outward, and if there will also be multilayer relaxations present. The aim of this paper is to contribute a theoretical answer to these questions from *ab initio* electronic structure calculations.

Experimental relaxations for the Al(001) surface were studied by low-energy electron diffraction (LEED),<sup>2,6–10</sup> medium energy electron diffraction (MEED),<sup>11</sup> medium energy ion scattering (MEIS),<sup>12</sup> MeV ion scattering (MeV IS),<sup>13</sup> and surface extended x-ray-absorption fine structure (SEXAFS).<sup>14</sup> The experimental evidence shows that the relaxation is small, but it is not completely conclusive if it is outward or inward (although the present consensus is outward). The experimental results for the first interlayer distance range from +2.6% (LEED) to less than –2.5% (MeV IS), and several papers report 0% relaxation for this surface.<sup>2,6–14</sup> Only two experimental works give evidence of multilayer relaxations.<sup>6,7</sup> With LEED being the most common technique used to study relaxations, it is worth mentioning briefly how these results are obtained. This is achieved by analyzing the dependence of the intensity of selected beams on the energy of the incident electrons: the so-called  $I(V)$  or  $I(\text{energy})$  curves. The atomic positions (and then the possible relaxations) must be inferred from the fitting of the experimental  $I(V)$  curves with some theoretical model. This model may contain multilayer relaxations or include only the topmost interlayer relaxation, or may not include the possibility of relaxation at all. If included, the corresponding relaxations are part of the fitting parameters to the experimental  $I(V)$  curves. When we analyze the papers of the literature on experimental relaxations of the Al(001), we may observe several inconsistencies. For example, one of the most cited papers quoting a 0% of relaxations for the Al(001) surface<sup>15</sup> did not include any relaxation parameter in the model. Soon later, the same authors included in the model the relaxation only for the surface layer obtaining evidence of a +2.5% expansion,<sup>9,10</sup> but it is still common to find theoretical as well as experimental papers (even from someone of the same authors<sup>8</sup>) referring only to the former 0% result. Another more recent and also frequently cited experimental result is the  $\sim 1.8\%$  expansion for the surface layer of Al(001) reported in Ref. 2. This value is an interpolation of their Fig 3 because the original value was not given in Ref. 2. Moreover, the original work for Al(001) cited in this reference is referred to as *to be published* and appears to us to have never been published. On the other hand, the possibility of multilayer relaxations was not considered up to the last two most recent LEED works. Moreover, the information about multilayer relaxations was not completely given in one work<sup>7</sup> and partially misinterpreted in the other.<sup>6</sup> Briefly, the experimental evidence of relaxations for the Al(001) surface, besides the spread of the results, appears to be incomplete. In particular, no experimental work has considered the possibility of very deep relaxations. In this paper, we will show that deeper relaxations, even if small, are still significant and should be considered experimentally.

From the theoretical point of view, a variety of semiempirical<sup>16–25</sup> as well as some *ab initio*<sup>4,26–31</sup> methods were used to study the relaxation of the Al(001) surface. Among the papers on semiempirical methods, we cite the electrostatic model of Finnis and Heine,<sup>16</sup> the effective-medium theory (EMT),<sup>17,18</sup> the embedded atom method (EAM),<sup>19,20</sup> the equivalent crystal theory,<sup>21</sup> the surface embedded Green's function (SEGF) methods,<sup>22,23</sup> the molecular dynamics method,<sup>24</sup> and the modified EAM (MEAM).<sup>25</sup> All

semiempirical methods report inward relaxations,<sup>16–24</sup> (ranging from –4.9% (EMT) to –1.0% (SEGF), except one paper<sup>25</sup> reporting outward relaxations of +0.8% (MEAM). The inward prediction is just the opposite of the last experimental result, raising the difficulties of semiempirical methods to correctly describe the small relaxation of the Al(001) surface. The *ab initio* methods have used mostly the pseudopotential approximation,<sup>26–31</sup> and there is only one paper using an all-electron linearized augmented plane wave (LAPW)<sup>4</sup> method, which is similar to what is used in the present paper. All these calculations predict an outward relaxation in agreement with the last experimental evidence. The magnitude of the relaxation for the surface interlayer goes from +1.89% to +0.5%, in fairly good agreement with the experimental results. However, there are important differences going to deeper relaxations. For example, the results for the relaxation of the second interlayer distance range from –0.3% to +4.12%; those for the relaxation of the third interlayer distances range from –0.1% to +2.96%; etc. Then, there is no consensus from *ab initio* calculations on the directions and magnitudes corresponding to deeper relaxations. Two recent papers using *ab initio* methods<sup>4,26</sup> explore in detail the convergence of the relaxations on the Al(001) surface as a function of the number of atomic layers considered in the slab used to simulate the surface. The pseudopotential work<sup>26</sup> considers slabs including up to 23 atomic layers, presenting results for the relaxation of the first four interlayer distances that show that the system is not fully relaxed yet because the absolute value still increases when going to deeper relaxations. A similar and even more pronounced problem was also found in a previous pseudopotential calculation.<sup>28</sup> The most recent *ab initio* paper<sup>4</sup> considers slabs containing up to 17 atomic layers, and the multilayer relaxations reported seems to be well relaxed. However, a 17 layer slab will probably not be sufficiently thick to capture the very deep relaxation pattern of the Al(001) surface, as we will show below and was also argued in Ref. 26. Moreover, in the last *ab initio* works,<sup>4,26–29</sup> the results are given without any indication of numerical error. This may be particularly problematic for very small relaxations, raising doubts about their reliability.

In this paper, we present results on multilayer relaxations for the Al(001) surface, obtained from *ab initio* electronic structure calculations, using the full-potential linearized/augmented plane wave plus local orbital (L/APW+lo) method as implemented in the WIEN2K code.<sup>32</sup> A slab of 23 atomic layers plus 20 empty layers to simulate the vacuum was used. Energy and forces are calculated self-consistently, and the geometry is varied to obtain the atomic positions with minimal energy and almost zero forces on all atoms. A careful analysis of the convergence of the results with the different parameters of the method was made. Error bars are reported as an indication of the precision of the calculation. After a complete relaxation, we found for the Al(001) surface an outward multilayer relaxation that penetrate well inside the material. The magnitude of the outward relaxation obtained for the topmost interlayer is in agreement with the experimental evidence. The pattern of the relaxation is a long-range damped oscillating wave, with several interlayer distances per oscillation and opposite to the most common

layer by layer oscillations obtained by LEED for most surfaces, for example, for the Al(110) surface.<sup>33</sup> Our results confirm that the relaxation propagates very deep into the bulk material and suggest that a new LEED  $I(V)$  fitting, including the possibility of relaxations up to the fourth interlayer, would be necessary. Our results also show that *ab initio* theoretical calculations need to be done on very thick slabs; otherwise, they may fail to capture the very deep, oscillating, and damped relaxation pattern shown by the Al(001) surface. A careful analysis of the charge density is made in order to understand the calculated multilayer relaxations. A comparison of charge density plots for the bulk, the unrelaxed slab, and the relaxed one is made for a plane perpendicular to the surface and for the surface plane itself. This analysis lets us understand the outward relaxation of the surface interlayer as related to the different electronic population of atomiclike  $p_{\parallel}$  and  $p_{\perp}$  surface orbitals, as was also argued (in a slightly different form) by Fall *et al.*<sup>29</sup> and numerically confirmed in our work. For both Al(001) and for the more compact Al(111) surfaces, the population imbalance is expected to be the dominant effect, compared with other simple metals, due to the strong character of atomiclike  $p$  orbitals of Al at the Fermi energy. A discussion of the possible origins of the multilayer relaxations will be made. In particular, Friedel-like charge density oscillations are put in evidence by subtracting the unrelaxed and bulk charge densities, and an analysis will be made considering the possibility of relaxations driven by these electronic oscillations. Finally, an analysis of the work function and surface energy calculations will be made. In order to calculate the surface energy, a careful analysis of the Al bulk energy calculated from the fcc symmetry or derived from slab calculations will be made. It will be shown that to a high precision almost the same value may be obtained as long as the same method-dependent parameters (except the  $k$  mesh and linearization energies) and thick slabs are used in the calculations.

The remainder of this paper is organized as follows. In Sec. II, the details of the calculational method and the used slabs are presented. Section III presents and discusses the results of the multilayer relaxations (Sec. III A), the forces on the unrelaxed slab (Sec. III B), the models for surface relaxations (Sec. III C), charge density (Sec. III D), work function (Sec. III E), and surface energy (Sec. III F). Final conclusions are presented in Sec. IV.

## II. CALCULATION METHOD

Density-functional<sup>34,35</sup> L/APW+lo calculations using the WIEN2K package<sup>32</sup> were employed to study the electronic structure and the atomic arrangement of the relaxed Al(001) surface. The atomic surface was simulated using a  $(1 \times 1)$  surface cell using a symmetric slab of 23 atomic layers plus 20 vacuum layers. The L/APW+lo method expands the Kohn-Sham orbitals in atomiclike orbitals inside the muffin-tin (MT) atomic spheres and plane waves in the interstitial region. For each particular atomic arrangement, the Kohn-Sham equations were solved using the generalized gradient approximation (GGA) of Perdew *et al.*<sup>36</sup> for the exchange-correlation potential. A detailed description of the method

may be found in Refs. 37 and 38. A very well converged electronic structure calculation (using the same basis set and GGA approximation) for the bulk fcc aluminum, as a function of the cell volume, shows the theoretical minimum nearly coincident with the experimental result. Then, the experimental fcc lattice constant ( $4.05 \text{ \AA} = 7.65 \text{ bohr}$ , Ref. 39) is used and a MT radius for all Al atoms of 2.65 bohr was considered. Inside atomic spheres, the basis set is split into core and valence states. The Al  $1s$  and  $2s$  states are considered as core states, and they are treated using only the spherical part of the potential but including all relativistic effects. They are assumed to have a spherically symmetric charge density totally confined inside the MT sphere. For the valence part, we have considered an expansion of the potential and the charge density in spherical harmonics up to  $L=6$ . The valence wave functions inside the spheres are expanded up to  $l=10$  partial waves. We have used a mixed basis set depending on the partial wave channel  $l$  and have used APW+lo functions for the  $s$ ,  $p$ , and  $d$  valence channels, with an additional local orbital (LO) for the Al  $2p$  semicore states and LAPW functions for the remaining partial waves ( $l=3-10$ ). In the interstitial region, a plane-wave expansion with  $R_{MT}K_{max}$  equal 8 is used, and the potential and the charge density are Fourier expanded with  $G_{max}=14$ . The modified tetrahedron method<sup>40</sup> was used to integrate inside the Brillouin zone (BZ), and a  $k$  sampling with a  $(36 \times 36 \times 1)$  Monkhorst-Pack<sup>41</sup> mesh in the full BZ was considered as satisfactory.

All the results presented in this paper were checked to have convergence with respect to the number of atomic layers, the number of vacuum layers, the number of  $k$  points inside the BZ, the number of plane waves used in the wave function expansions, and the number of Fourier coefficients used to expand the potential and charge density in the interstitial region. For each particular geometry and set of parameters, self-consistent electronic solutions were obtained, well converged on the total energy, on the charge inside all the atomic spheres, and on the forces on all atoms (0.01 mRy/bohr). The calculations of the forces include the Hellman-Feynman contribution and the incomplete basis set (Pulay forces) correction for valence as well as core wave functions. The forces were calculated for all atoms in all layers of the slab, except for the atom of the central layer, whose position was kept fixed by symmetry. The atomic positions were then relaxed according to the Port version of the quasi-Newton minimization method, repeating the process of electronic self-consistent calculations and relaxation of atomic positions until the forces on every atom drop below 0.15 mRy/bohr. Table I summarizes the structural as well as the method-dependent parameters used in this work.

In Table II, we present our results for the multilayer relaxations of Al(001), including, as error bars, an estimation of the numerical precision of our results. The error bars were obtained doing further calculations up to the complete relaxed system is obtained again, increasing (one at a time) the number of  $k$  points (duplicating them in the full BZ), the number of plane waves used to expand the wave function in the interstitial region ( $R_{MT}K_{max}$  parameter from 8 to 9), the number of plane waves in the expansion of potential and charge density ( $G_{max}$  from 14 to 16), the number of atomic

TABLE I. Structural and L/APW+lo dependent parameters used in this work. (LO: local orbital, PW: plane waves, WF: wave function, IBZ: irreducible Brillouin zone, and AS: atomic sphere).

Structural parameters	
$a_{fcc}=7.65$ bohr (4.05 Å)	
(1 × 1) slab of 23 atomic+20 empty layers	
$a_{slab}=b_{slab}=(\sqrt{2}/2)a_{fcc}=5.41$ bohr	
$c_{slab}=160.72$ bohr	
$\alpha_{slab}=\beta_{slab}=\gamma_{slab}=90^\circ$	
$d_{i,i+1}(\text{bulk})=a_{fcc}/2=3.83$ bohr	
Vacuum size=76.53 bohr	
L/APW+lo dependent parameters	
xc potential: PBE-GGA (Ref. 36)	
$R_{MT}=2.65$ bohr	
Inside MT spheres	Interstitial region
Basis set:	
Core: Al 1s and 2s	PW expansion for WF:
Semicore: Al 2p treated as LO	$R_{MT}K_{max}=8$
Valence: s, p, and d, APW+lo	
$l=3$ to $l=10$ channels: LAPW	
Potential and charge density expanded in spherical harmonics up to $L=6$	Potential and charge density expanded in PW up to $G_{max}=14$
BZ sampling: $36 \times 36 \times 1$ (171 $k$ points inside the IBZ)	
scf convergence criteria for fixed nuclear positions:	
forces on all atoms converged to 0.01 mRy/bohr	
Convergence criteria to stop relaxation search:	
forces on all atoms lesser than 0.15 mRy/bohr	

layers (21 to 23), and the size of the vacuum region (10 layers to 20 layers). The error bars correspond to the maximum deviation of the result obtained with the parameters given in Table I due to any of these variations.

### III. RESULTS AND DISCUSSION

#### A. Multilayer relaxations

We started the calculations using an unrelaxed slab with all atoms in their bulk positions. The resulting forces and charge densities of this system will be used finally to compare and understand the results obtained for the completely relaxed slab.

Due to the symmetry of the chosen (1 × 1) unit surface cell, only relaxations normal to the surface are possible. When all atoms are relaxed until the forces on them are below 0.15 mRy/bohr, we obtain a long-ranged multilayer relaxed surface. In Table II, we report the relaxations  $\Delta d_{i,i+1}$  calculated in this work for each interlayer of the 23 layers (23L) slab, together with the results from other *ab initio* calculations, and in Table III, we collect the experimental information on relaxations for the Al(001) surface. To better

analyze the obtained results, we first explore the available experimental information. LEED, MEED, MEIS, MeV IS, and SEXAFS experiments were made to determine these relaxations. Whereas four different LEED experiments reported an outward relaxation,<sup>2,6-8</sup> MEED<sup>11</sup> and MeV IS<sup>13</sup> gave evidence of an inward relaxation. MEIS<sup>12</sup> and SEXAFS<sup>14</sup> experiments indicated a nonrelaxed surface, but with an experimental error bar so that practically all other experimental results are compatible with them. From these results, we may conclude that the experimental relaxation of the Al(001) surface is small, but the experimental evidence is not conclusive if this small relaxation is outward or inward. Considering only the latest LEED results,<sup>2,6,7</sup> the present consensus is that the Al(001) surface relaxes outward. From Table III, we may observe only two experimental works<sup>6,7</sup> where multilayer relaxations were considered. These studies have included up to the third interlayer ( $\Delta d_{3,4}$ ) parameter, and we note that the second interlayer distance was not given in Ref. 7. In both studies, the clean Al(001) surface was not the main issue, but only the substrate to study adsorbates.<sup>6,7</sup> Further inner relaxations were not considered in any experimental work.

When analyzing our relaxations of the Al(001) surface presented in Table II, we observe a multilayer damped wave pattern, which is better shown in Fig. 1 where the calculated interlayer relaxations, including the error bars, are plotted as a function of the particular interlayer considered. Figure 1 clearly displays a multilayer relaxation with a damped relaxation wave. It has its maximum amplitude at the surface interlayer and approaches zero at the center of the slab. It is interesting to note that the oscillatory character of this damped wave takes several layers instead of the most common behavior of oscillating layer by layer, as it is the case, for example, for the Al(110) surface.<sup>33</sup> In Fig. 1, we can see that the three topmost interlayers show an outward relaxation, whereas well inside the slab, the fourth to seventh interlayers relax inward, and the following interlayer relaxes outward, ending with practically no relaxation when approaching the center of the slab, that is, the bulk of the material.

In particular, a  $\Delta d_{1,2}=(1.51 \pm 0.06)\%$  outward relaxation was obtained for the surface interlayer, in fairly good agreement with the four LEED experimental results (see Table III).<sup>2,6-8</sup> This theoretical value is also inside the range given by the error bars in MEIS<sup>12</sup> and SEXAFS<sup>14</sup> experiments, but it is in disagreement with the MEED<sup>11</sup> and MeV IS<sup>13</sup> experiments that report an inward relaxation. Our result for the relaxation of the second interlayer,  $\Delta d_{2,3}=(0.42 \pm 0.02)\%$ , is bigger and just outside the range of the only available experimental result.<sup>6</sup> For the third interlayer, we predict an almost zero outward relaxation  $\Delta d_{3,4}=(0.03 \pm 0.02)\%$ , falling inside the experimental range for one experiment,<sup>6</sup> but just outside the range for the other experimental result,<sup>7</sup> both centered at a  $-0.5\%$  inward relaxation (see Table III).

When compared with other *ab initio* methods, our 1.51% relaxation for the surface interlayer agrees with those of the two recent calculations of Da Silva (1.598%, Ref. 4) and Chis and Hellsing (1.50%, Ref. 26) and, to a lesser extent, with previous pseudopotential results (see Table II). We would like to emphasize that all the *ab initio* calculations

TABLE II. Multilayer relaxations for the Al(001) surface,  $\Delta d_{i,i+1}$ , in % of the bulk interlayer distance, from theoretical *ab initio* calculations.  $\Delta d_{i,i+1}$  is defined in Eq. (1). *NL* indicates the number *N* of atomic layers used in the slab by the respective calculation, and pp means pseudopotential method. We refer to Sec. II of this work, to see how the error bars of our theoretical results were estimated. [For semiempirical calculations on Al(001) we refer to Refs. 16–25. For  $\Delta d_{1,2}$ , the semiempirical predicted results are mainly inward, except Ref. 25, where a 0.8% value was obtained.]

$\Delta d_{i,i+1}$ %	23L-L/APW+lo	17L-LAPW	23L-pp	7L-pp	9L-pp	8L-pp	15L-pp	15L-pp
	GGA (This work)	GGA (Ref. 4)	LDA (Ref. 26) <sup>a</sup>	GGA (Ref. 27)	LDA (Ref. 28)	LDA (Ref. 29)	LDA (Ref. 30) <sup>b</sup>	LDA (Ref. 31)
$\Delta d_{1,2}$	1.51±0.06	1.598	1.50	0.5	1.89	0.9	1.2±0.4	0.7±0.3
$\Delta d_{2,3}$	0.42±0.02	0.436	1.19	-0.3	4.12	0.4	0.2±0.4	0.2±0.3
$\Delta d_{3,4}$	0.03±0.02	-0.020	0.64		2.96		-0.1±0.4	0.4±0.3
$\Delta d_{4,5}$	-0.40±0.01	-0.682	0.66		2.94			
$\Delta d_{5,6}$	-0.30±0.04	-0.564						
$\Delta d_{6,7}$	-0.20±0.04	-0.085						
$\Delta d_{7,8}$	-0.05±0.02							
$\Delta d_{8,9}$	0.06±0.02							
$\Delta d_{9,10}$	0.00±0.05							
$\Delta d_{10,11}$	-0.02±0.07							
$\Delta d_{11,12}$ <sup>c</sup>	-0.04±0.01							

<sup>a</sup>The experimental values quoted in Table I of Ref. 26 are incorrect. They refer to our Ref. 7, and the correct values are included in Table III of the present work.

<sup>b</sup>No explicit indication was given on how the error bars were calculated.

<sup>c</sup>Layer 12 simulated the bulk and was kept fixed in our calculation.

agree in the prediction of an outward relaxation for the Al(001) surface, in accord with the present accepted experimental result. For the second interlayer, we obtain a 0.42% value, in agreement with the LAPW result of Da Silva (0.436%, Ref. 4) and the pseudopotential result of Fall *et al.* (0.4%, Ref. 29) but in disagreement with the pseudopotential results of Chis and Hellsing (1.19%, Ref. 26) and Zheng *et al.* (4.12%, Ref. 28) and in strong disagreement with the inward prediction of Borg *et al.* (-0.3%, Ref. 27). Going

further inside, our 0.03% value for the third interlayer still compares reasonably well with the result of Da Silva<sup>4</sup> (even if he predicted an inward relaxation of -0.020%, the absolute value approached zero, same as our value), but disagrees with those of Chis and Hellsing (0.64%, Ref. 26) and Zheng *et al.* (2.96%, Ref. 28) obtained using the pseudopotential approximation. We predict an inward relaxation for the fourth interlayer:  $\Delta d_{4,5} = -0.40\%$ . This result is in qualitative agreement with that obtained by Da Silva, whose numerical

TABLE III. Experimental relaxations,  $\Delta d_{i,i+1}$ , for Al(001) surface, given in % of the bulk interlayer distance.  $\Delta d_{i,i+1}$  defined in Eq. (1).

$\Delta d_{i,i+1}$ (%)	LEED 100 K (Ref. 6) <sup>a</sup>	LEED 100 K (Ref. 7)	LEED <i>T</i> not given (Ref. 2)	LEED 300 K (Ref. 8)	MEED 77 K (Ref. 11)	MEIS 300 K (Ref. 12)	MeV IS 300 K (Ref. 13)	SEXAFS 300 K (Ref. 14)
$\Delta d_{1,2}$	2.0±0.8	+2.6±0.2	~1.8 <sup>b</sup>	(0,4.9) <sup>c</sup>	(0,-1.5) <sup>d</sup>	0±5	(0,-2.5) <sup>e</sup>	0.0±2.5 <sup>f</sup>
$\Delta d_{2,3}$	1.2±0.7	Not reported						
$\Delta d_{3,4}$	-0.5±1.0 <sup>g</sup>	-0.5±0.4						

<sup>a</sup>In Table II of this reference, the value given as  $d_{\text{Al}_7\text{-Al}_3}$  of Ref. 17 (our Ref. 7) corresponds, in fact, to the  $d_{\text{Al}_3\text{-Al}_4}$  distance. Then, the comparison authors of this reference made in their Table II is partially incorrect.

<sup>b</sup>Interpolated from Fig. 3 of Ref. 2. Original reference stated as *to be published*.

<sup>c</sup>Authors state that the interlayer distance is equal to that of the bulk within approximately 0.1 Å (4.9% of relaxation), with a slight indication of expansion. Previous results of the same group (Refs. 9 and 10) indicate an expansion of 2.5%.

<sup>d</sup>Authors present their result as 0%, but for a nonexhausted fitting of parameters, they obtain an experimental relaxation of -1.5%.

<sup>e</sup>The original result states that the relaxation is inward and less than -0.05 Å.

<sup>f</sup>The authors estimated the error as 0.05 Å (2.5%).

<sup>g</sup>Original value given as (2.01±0.02) Å in Table I of Ref. 6

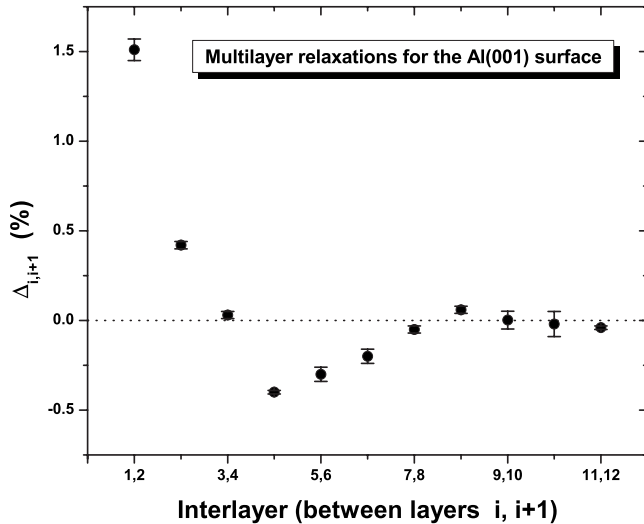


FIG. 1. Multilayer relaxation as a function of the respective interlayer, going from the surface (left) to the bulk (right). Numerical values and error bars given in Table II.

value ( $-0.682\%$ , Ref. 4) differs by 70% from ours and is strongly in disagreement with pseudopotential results that predict an expansion of  $0.66\%$  (Ref. 26) or  $2.94\%$  (Ref. 28). For the two further inside relaxations ( $\Delta d_{5,6}$  and  $\Delta d_{6,7}$ ), we may compare our results only with those given by Da Silva, both obtaining inward relaxations for these two interlayers, but with numerical differences greater than 50% (see Table II). In this way, a clear difference emerges between the results obtained using pseudopotentials or LAPW-based methods. While the surface interlayer relaxation may be predicted correctly by both kind of methods, the inner multilayer relaxations show even qualitative differences (except with fairly old calculations in Ref. 30). All except one pseudopotential calculations have used the LDA approximation. However, the only pseudopotential calculation that uses the GGA approximation, predicts an inward  $\Delta d_{2,3}$  relaxation in strong disagreement with LAPW-based methods. With the present work and that of Da Silva being both LAPW-based methods, it is worth mentioning what the differences between them are. The main differences are the size of the used slab ( $23L$  in our work compared to  $17L$ ) as well as the basis functions used to expand the wave functions in the vacuum region (plane waves in our work compared to plane waves times exponential decay functions). On the other hand, when comparing our calculation with the pseudopotential results of Chis and Hellsing,<sup>26</sup> we note that both works have used a slab of  $23L$ . However, as we can see in Table II, the relaxation results of this work are far from a complete relaxation of the surface. We consider that a surface has achieved complete relaxation when the multilayer relaxation goes to, and remains, zero when considering successive inner layers. Besides a reasonable big vacuum region, the appropriate size of the atomic layers in the slab is crucial to capture the very deep multilayer relaxation wave of the Al(001) surface. As an example of this, we present our well converged calculations for an  $11L$  slab, for which we have obtained the following results:  $\Delta d_{1,2}=1.41\%$ ,  $\Delta d_{2,3}=0.35\%$ ,  $\Delta d_{3,4}=0.05\%$ , and  $\Delta d_{4,5}=-0.43\%$ . These values compare well with those

obtained for the  $23L$  slab included in Table II. However, if we only consider the  $11L$  slab (a common size still used in the literature), we cannot explain why the relaxation observed for the  $\Delta d_{4,5}$  becomes inward and with a non-negligible value, instead of going to zero. Only a bigger slab allows us to understand that this inward relaxation is just a part of the damped, oscillating multilayer relaxation wave, characteristic of the Al(001) surface. This multilayer relaxation wave is not found in any pseudopotential calculations but is sketched in the results of Da Silva and is completely confirmed in our work.

Finally, when the experimental results on relaxations are compared themselves (see Table III), we realize that new experiments on the Al(001) surface would be desirable. New LEED experiments should incorporate the possibility of very deep relaxations, such as those predicted in this work, i.e., the fourth ( $\Delta d_{4,5}$ ) or fifth ( $\Delta d_{5,6}$ ) interlayer relaxations. When multilayer relaxations are taken into account, the new interpretation based on the same experimental data may be different, even for the surface interlayer. One example of this behavior is given by the Fe(111) surface, when the *same* LEED  $I(V)$  curves were fitted without and including multilayer relaxations, as was documented in Ref. 42. New ion scattering and SEXAFS experiments on Al(001) would also be welcome to definitively determine the outward relaxation character of this surface.

## B. Forces for the unrelaxed slab

It is normally assumed that the relaxed interlayer distances correlate with the direction of the forces obtained for the unrelaxed slab. In Table IV, we present the magnitude of the forces normal to the surface obtained in this work for the unrelaxed slab, where a positive value indicates a force directed toward the surface and a negative one toward the bulk.

When we compare the forces of Table IV with the values of the literature, even if all works correctly predict an outward relaxation for the topmost interlayer distance, some noticeable differences may be observed. For example, we have obtained  $2.93$  mRy/bohr for the force on the surface atom, whereas a four times smaller value can be seen in Fig. 3 of Ref. 26, but a twice as large value ( $6.52$  mRy/bohr) was obtained in Ref. 28. When considering the inward force on the second atomic layer, the comparison becomes even worse: our  $-2.19$  mRy/bohr value must be compared with almost zero of Ref. 26 and the strong outward pointing force of  $5.99$  mRy/bohr obtained in Ref. 28. These discrepancies may be attributed to the differences between the pseudopotential method employed in Refs. 26 and 28, and the all-electron method we have employed in this work.

From the values of Table IV, we may understand why the topmost interlayer distance relaxes outward,  $d_{4,5}$  relaxes inward, and  $d_{8,9}$  relaxes outward. In all these cases, opposite forces are acting on the respective two neighboring layers, and most probably they will be responsible for expansion/contraction of the corresponding interlayer distances. However, it is not obvious from the values of the forces acting on atoms of the second and third layers that the final result will be an expansion of their interlayer distance. The same is

TABLE IV. Total forces on atoms at the indicated layer obtained for the 23L unrelaxed slab (in mRy/bohr). Layer 1: surface layer; layer 12: bulk layer. A positive (negative) value indicates an outward (inward) force.

Layer	1	2	3	4	5	6
	2.93	-2.19	-0.81	-0.99	0.16	0.22
Layer	7	8	9	10	11	12
	0.26	0.13	-0.17	-0.13	-0.07	0.00

valid for other pairs of consecutive planes, which have forces in the same direction. The conclusion would be that the forces calculated for atoms in the unrelaxed slab correlate only with the relaxed interlayer distances that give the maximum amplitudes (in absolute value) of the oscillatory damped relaxed wave of Fig. 1.

We may also analyze if some correlation exists among the forces of Table IV and the final relaxed positions of atoms at the different layers. The final relaxed positions show that this correlation is valid for all atomic layers except the fifth, sixth, and seventh layers, whose final coordinates are found slightly on the opposite side (with reference to the unrelaxed layers) of the original directions of the forces before relaxation. Thus, the dynamical adjustment of the forces in the relaxation process may lead to relaxations opposite to the original directions for the nonrelaxed system, raising the importance of a careful relaxation of all positions.

As a consequence, we would like to stress the importance to distinguish between the relaxation of *the interlayer distances* and the relaxation of *the single-atomic layer positions*, both compared with their respective bulk values. Whereas the former follows the oscillating multilayer relaxation given in Fig. 1, the latter shows that the surface layer relaxes outward, whereas the 2nd to the 11th layers relax inward, with the only exception of the 8th layer that continues to relax outward with respect to the unrelaxed positions.

### C. Models for surface relaxations

The outward relaxations of the Al(001), as well as the Al(111) surfaces, are commonly referred to as *anomalous* because they relax in the opposite way as do other simple metal surfaces (such as Cu or Ni low-index surfaces<sup>2</sup>). Analogously, the normal pattern for a multilayer relaxation is a layer by layer oscillation [as in the case, for example, for the Al(110) and Al(111) surfaces]. In this way, the Al(001) surface appears to be twice anomalous because it not only relaxes outward, but also does that with a long wavelength oscillating pattern of multilayer relaxation.

We would like to understand why a given metallic low-index surface relaxes inward or outward, what the driving forces that generate multilayer relaxation (if present) are, and why, in some cases, relaxations occur in other than the most common layer by layer oscillation pattern.

Different proposals were presented in the literature to account for the observed experimental relaxations of simple metals. The electrostatic model of Finnis and Heine (Ref. 16), based on the Smoluchowski (Ref. 43) idea of smoothing

of charge, was the first model to explain the inward relaxation observed for simple metals as well as the correlation of relaxations with the compactness of surfaces (the more open a surface is, the more important charge smoothing and the corresponding surface relaxations will be). However, this model, as well as others based on it, is not able to explain neither the outward relaxations nor the presence of multilayer relaxations. In order to understand the presence of outward relaxations, Feibelman<sup>44</sup> proposed a chemical model based on promotion-hybridization ideas. This author was able to explain the experimental large outward relaxation of the Be(0001) surface, as well as to predict significant inward relaxations for the Ti(0001) and Zr(0001) surfaces. This model, however, cannot be applied properly to deal with deeper multilayer relaxations. In order to incorporate the latter, Cho *et al.*<sup>45</sup> proposed that multilayer relaxations in free-electron-like metals may arise from Friedel oscillations of the charge density for bulk-truncated surfaces. The so-called Friedel oscillations were first obtained by Friedel as the response of a homogeneous Fermi gas when screening the presence of an impurity.<sup>46</sup> They are a consequence of the Fermi-Dirac statistic obeyed by the electrons, and Friedel found that the screening of an impurity generates long-ranged charge density oscillations. Friedel oscillations were also found in the context of the density-functional theory by Lang and Kohn<sup>47</sup> as the response to a metallic surface on the jellium model. The wavelength of the oscillations was one-half of the Fermi wavelength  $\lambda_F/2 = \pi/k_F$ , with  $k_F$  being the Fermi momentum. Moreover, when the jellium model is replaced by a real crystalline potential, the Friedel oscillations can still be found, as was shown by Cho *et al.*<sup>45</sup> for the Mg(10 $\bar{1}$ 0) and Al(110) surfaces, by Staikov and Rahman<sup>48</sup> for three different surfaces of Mg, and by Wachowicz and Kiejna<sup>49</sup> for Be(0001) and Mg(0001) surfaces. In these examples, inward as well as outward multilayer relaxations were successfully explained. In all cases, unidimensional plots of the  $[\rho(z) - \rho_0]/\rho_0$  were given as a function of  $z$  (the normal to the surface), with  $\rho(z)$  being the calculated charge density for the *unrelaxed* slabs averaged over planes parallel to the surface along the slabs, and  $\rho_0$  the mean charge density for the corresponding bulk. The  $xy$ -averaged charge density difference was found to oscillate with an almost layer by layer pattern with a wavelength that approximates the  $\lambda_F$  of the corresponding material. In this way, Friedel oscillations, like those found for the jellium model, are made evident for real crystals, but at the cost of losing the detailed information included in the complete, nonaveraged charge density. In this electrostatic model based on Friedel oscillations,<sup>45</sup> the charge density redistribution obtained for the unrelaxed slab is still insufficient to completely screen the positive ions. Further atomic relaxations, with forces according to the accumulation or depletion regions due to the Friedel oscillations, are necessary to complete the screening process, ending in a stable structure. For all previous studied cases, the  $xy$ -averaged charge density for the relaxed structure still exhibits a layer by layer pattern similar not only to that of the unrelaxed slab but also to that corresponding to the multilayer relaxation pattern. These results show a correlation between the charge density and the multilayer relaxation

pattern, both basically formed by a pattern of layer by layer oscillations. The validity of the model depends on the free-electron-like character of valence electrons at the surface region. For a more covalentlike character, for example, that found for the Be(10 $\bar{1}$ 0) surface,<sup>50</sup> the relaxation model based on Friedel oscillations is no longer appropriate. For these cases, the Feibelman chemical picture based on bond-order bond-length correlations<sup>44</sup> would be more suitable. Finally, a different model was proposed to explain the presence of multilayer relaxations by Allan and Lannoo,<sup>51</sup> who concluded that multilayer relaxations are related to solutions of zero frequency in the complex phonon structure. This model, developed in the tight binding context, has the virtue to naturally explain damped deep multilayer relaxations, lacking in predicting the outward or inward relaxations for the surface interlayer. The authors proposed a solution formed by an oscillatory function times an exponentially damped function, whose parameters were fitted using a force field model, to the complex bulk phonon dispersion curve. The proposed solution also include a prefactor that is fitted to the experimental inward or outward relaxation for the surface interlayer. It is interesting to note that this model is based only on the change in the vibrational properties that occurs when a surface is formed, while all the previous models are based on the change on the electronic distribution for the same situation. Most probably, both mechanisms are present and strongly coupled in real surfaces.

As a conclusion, at present, there is no unique model to explain the experimentally observed inward or outward multilayer relaxations of simple metals. Moreover, for low-index metallic surfaces, no model seems to have explored the possibility of an oscillating relaxation pattern with a wavelength of several layers, such as that obtained in Fig. 1 for the Al(001) surface. Based on our results for the multilayer relaxations of the Al(001) surface, we would discard, in principle, the Finnis and Heine based models as well as the chemical picture of Feibelman because all of them predicts an inward relaxation for this surface. Friedel oscillation based methods as well as the zero frequency solutions in the complex phonon structure are retained as possible mechanisms to account for the calculated multilayer relaxations. In Sec. III D, we will explore the presence of Friedel oscillations, analyzing in detail the charge density, and we will discuss the possibility of electronically driven relaxations for the Al(001) surface.

## D. Charge density

### 1. Plane perpendicular to the surface

In order to understand the possible mechanism behind the obtained relaxations, we have analyzed the problem in two steps. The first one is to investigate how the electrons relax for fixed bulklike atomic positions when the surface is formed; i.e., we compare the changes in the valence charge density between the bulk and the unrelaxed slab. In the second step, we study the further electronic relaxations for the fully relaxed surface, i.e., the valence charge density changes from the unrelaxed to the relaxed slab. Figures 2(a)–2(c) show the valence electron distribution for the (100) plane

perpendicular to the surface of the bulk, the unrelaxed, and the relaxed surfaces, respectively.

The analysis of the bulk density [Fig. 2(a)] reveals an accumulation of valence charge in the bonds between first nearest neighbors (nn). It is characterized by the 0.20 and 0.21  $e/\text{\AA}^3$  contour levels located along the nn directions between two atoms. When the surface is formed but the atoms still keep their bulk positions [Fig. 2(b)], the electronic charge density relaxes in order to screen the newly formed defect (the surface). Consequently, Fig. 2(b) shows for the surface interlayer along the nn directions that the charge density has lost the 0.21  $e/\text{\AA}^3$  contour level near the surface atoms, but is still keeping those near the second atomic layer. Moreover, for deeper interlayers of the unrelaxed slab, the 0.21  $e/\text{\AA}^3$  contour level is still always present. As a consequence, the valence charge density is no longer symmetrical for the surface interlayer of the unrelaxed slab, generating a different electronic screening for the ions located at the planes defining this interlayer. This different screening is the origin of the forces that push the ions at the surface outward and those belonging to the subsurface inward. When the atomic positions are relaxed [Fig. 2(c)], the final electronic charge density becomes again almost symmetrical between the two topmost atomic layers, but the charge density characterized by the 0.21  $e/\text{\AA}^3$  contour line is not present anymore. Again, for deeper interlayers of the relaxed slab and in spite of some minor changes, the 0.21  $e/\text{\AA}^3$  contour levels are always present. In both Figs. 2(b) and 2(c), the valence charge densities for atoms further away from the surface become more and more similar to the bulk charge density of Fig. 2(a). In Fig. 2(b), we may also observe an accumulation of electronic charge directly on top of each surface atom that is also preserved after the atomic relaxations [Fig. 2(c)]. For the unrelaxed case, this gives rise to an additional outward force acting on the atoms of the surface layer, whereas in the relaxed case, it is balanced after the redistribution of the electronic charge.

It is interesting to compare the charge densities obtained for the Al(001) surface with those obtained by Ho and Bohnen<sup>52</sup> for the Al(110) surface. Of course, the particular planes are different, but they are all perpendicular to their respective surfaces, letting us understand a bit more the different relaxations exhibited by these surfaces. This comparison is useful, especially when we remember that the Al(110) surface relaxes inward whereas Al(001) relaxes in the opposite direction. For the unrelaxed Al(110) geometry, Ho and Bohnen (see Figs. 1 and 2 of Ref. 52) found that the charge density among atoms defining the first interlayer is fairly uniform, whereas we found the opposite for the Al(001) surface. They observed, for the unrelaxed slab, a piling up of electrons directly on top of each surface atom, similar to what we found for the Al(001) case. After relaxation, they reported an increase of charge between nn atoms inside the surface interlayer, again in the opposite way as was found for the Al(001) surface. The pileup of electrons on top of the surface atoms remains almost unchanged after atomic relaxation for both Al(110) and Al(001) surfaces. The different open nature of each surface allows electrons to relax in a different way to screen the surface. The extra electronic charge in between the topmost layers after atomic relaxation



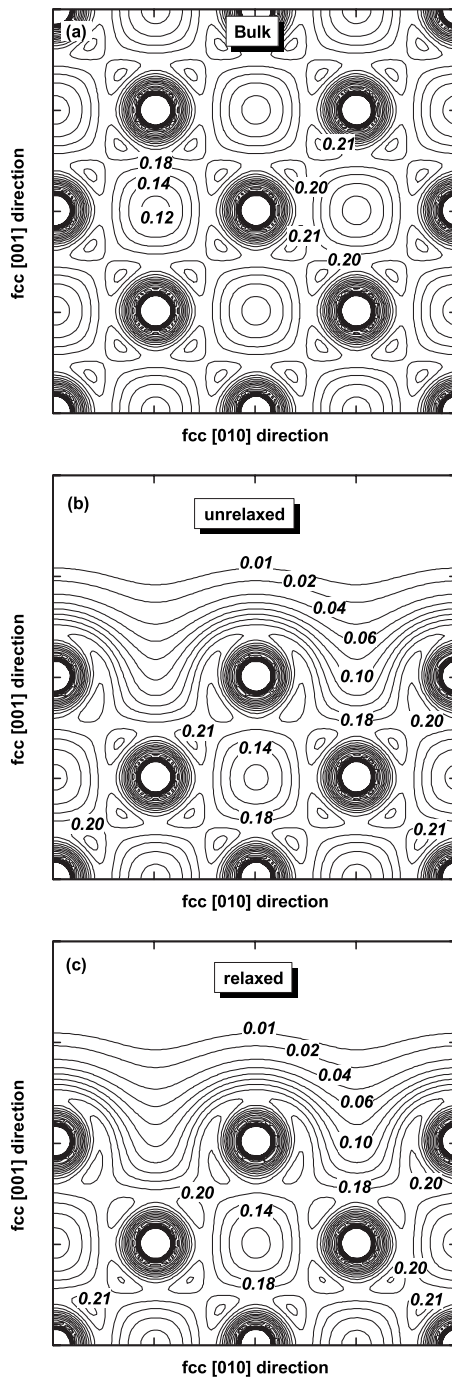


FIG. 2. Contour plots of the valence charge density for the (100) plane of the (a) bulk, (b) unrelaxed, and (c) relaxed  $23L$  slabs. Contour levels in  $e/\text{\AA}^3$  as labeled in the figures.

is compatible with an inward relaxation, as measured for the Al(110). On the other hand, the change from a nonsymmetrical to a symmetrical but lower charge density is compatible with an outward relaxation, such as those found for Al(001). Thus, the charge density analysis provides natural insight to characterize the inward relaxation of Al(110) as well as the outward relaxation of the Al(001) surface.

Following the analysis of the charge density for the Al(001) surface, we present in Figs. 3(a)–3(c) the valence charge density differences for the unrelaxed slab minus the

bulk, the relaxed minus unrelaxed slabs, and the relaxed slab minus the bulk, respectively. In order to visualize that differences occur well inside the material, we have included in Fig. 3 up to five atomic planes from the surface. An analysis of Fig. 3(a) shows, as expected, that the major differences between the unrelaxed slab and bulk occurs at the surface and inside the first interlayer. In this region, we may understand why the  $0.21 e/\text{\AA}^3$  contour level is missing near the surface atoms. Indeed, there is a quite localized charge accumulation around the surface atoms within the surface plane. Figure 3(a) also shows a charge accumulation between atoms at the second layer and an important depletion of charge within the first interlayer (between the two top atomic layers). This charge redistribution naturally explains the opposite forces given in Table IV for the atoms at the two topmost layers, which drive the outward relaxation of the Al(001) surface. For deeper interlayers, the difference shows only some small charge oscillations which do not alter the presence of both  $0.21 e/\text{\AA}^3$  contour levels in the nn directions. From Fig. 3(b), we can see in the region near the atoms a dipolar charge difference that can be explained by the movement of atoms in the relaxation process. We may also observe that after a complete relaxation some extra charge is placed on top of the surface and that for deep interlayers some oscillations in the charge density are again present. These oscillations, together with those found in Figs. 3(a) and 3(c), could play an important role for the long wavelength multilayer relaxations, as will be discussed in more detail later in the context of Friedel oscillations.

## 2. Surface plane

All the above discussion corresponds to a plane perpendicular to the Al(001) surface. In Fig. 4(a), we present charge density plots within the surface plane for the unrelaxed slab. A comparison between this charge density and the bulk [Fig. 2(a)] shows that when the surface is formed (and atoms still keep their bulk positions), electrons pile up in the nn directions within the surface plane. This is better shown in the difference density plotted in Fig. 4(b). The extra charge is found mostly between the nn surface atoms and comes in part from the surface interlayer region and in part from a redistribution of charge within the plane itself. When we relax the slab, the relaxed charge density (not shown) is nearly the same as that for the unrelaxed slab [Fig. 4(a)]. Thus, for the surface plane, an almost complete electronic rearrangement occurs already when the surface is formed (unrelaxed case), and further atomic relaxations do not modify the charge density in the surface plane significantly.

## 3. Partial charges

The extra charge between nn atoms at the surface plane and the depletion of charge between the surface atoms and its nearest neighbors at the second layer mean that we have an asymmetry in the population of the Al  $3p$  orbitals of the surface atom. In Table V, we present the calculated partial charges of the  $p_{\parallel}$  and  $p_{\perp}$  states obtained for the first five atomic layers for the unrelaxed and relaxed  $23L$  slabs. From these values, we can see that for the surface atoms the popu-

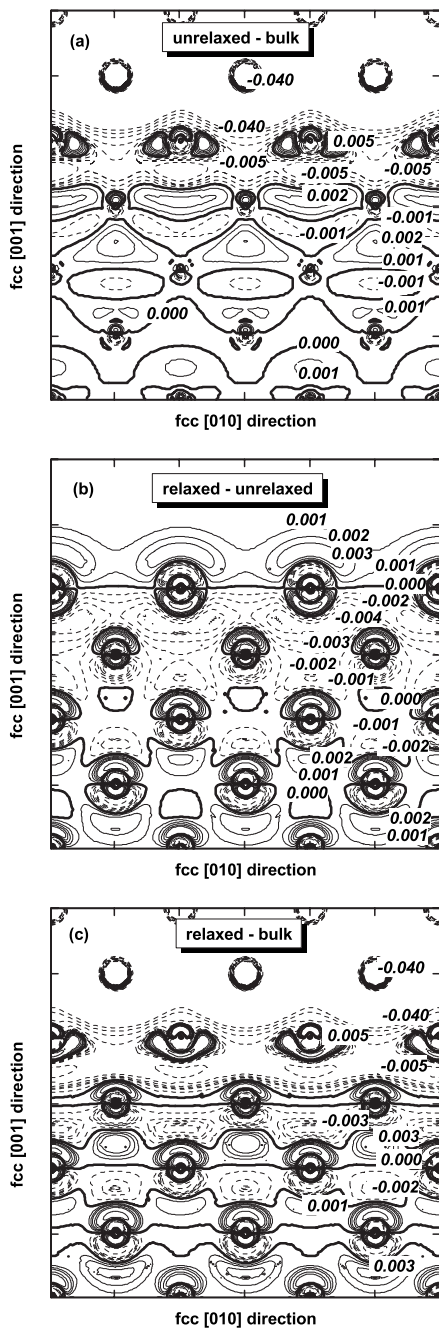


FIG. 3. Contour plots of the valence charge density differences for the (100) plane of (a) unrelaxed 23L slab minus bulk, (b) relaxed minus unrelaxed 23L slabs, and (c) relaxed 23L slab minus bulk. Contour levels go from  $-0.04$  to  $0.04 e/\text{\AA}^3$ , in steps of  $0.01 e/\text{\AA}^3$ , while those between  $-0.005$  and  $0.005 e/\text{\AA}^3$  were taken in steps of  $0.001 e/\text{\AA}^3$ . Solid (broken) lines indicate positive (negative) values. The thicker solid line indicates the zero contour level. The decimal point of the contour labels are placed exactly on the corresponding contour line.

lation of  $p_{\parallel}$  and  $p_{\perp}$  states is smaller than for the bulk (by about  $0.04e^-$ , and  $0.09e^-$ , respectively). In addition, the  $p_{\parallel}$  occupation is  $0.05e^-$  bigger than the corresponding  $p_{\perp}$  charge, while it is, of course, identical for the bulk. The changes between the unrelaxed and relaxed slabs are minor, indicating that the major charge redistribution for the Al(001)

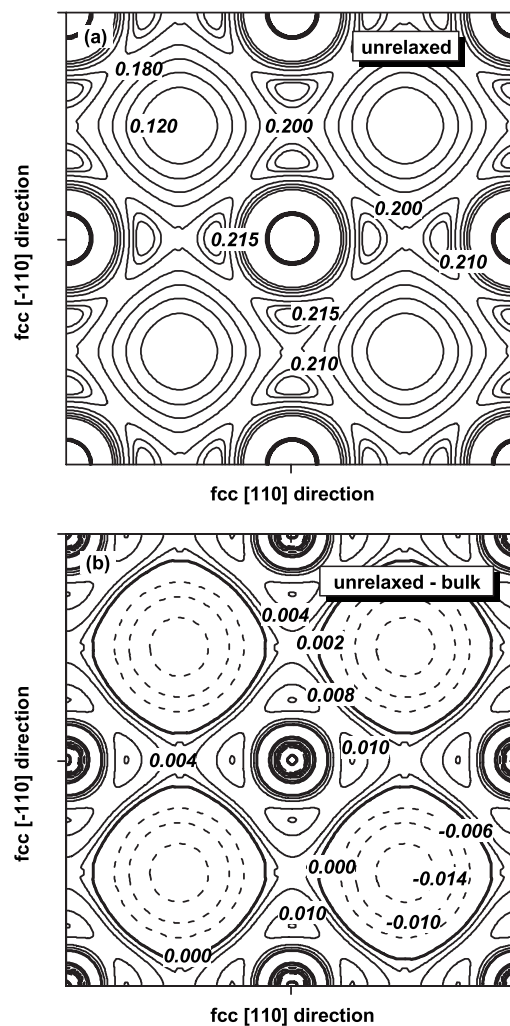


FIG. 4. Contour plots of the valence charge density ( $e/\text{\AA}^3$ ) for the Al(001) surface plane for (a) the unrelaxed slab and (b) the difference unrelaxed slab minus bulk. Solid (broken) lines indicate positive (negative) values.

surface occurs when the surface is formed and the atomic relaxations play only a minor role in these  $p$  charge redistribution. For the subsurface atoms, the differences between  $p_{\parallel}$  and  $p_{\perp}$  states are an order of magnitude smaller and the total  $p$  charge is very similar to the bulk. The conclusion is that for atoms at the surface layer, parallel  $p_{\parallel}$  states become energetically more favorable than the perpendicular  $p_{\perp}$  states, which extend into the vacuum and other regions of higher potential. This result, obtained for the outward relaxation of the Al(001) surface, could be extended and related to the compactness of the Al(111) and Al(110) surfaces. For example, for the most compact Al(111) surface, the increase of the atomiclike  $p_{\parallel}$  with respect to the  $p_{\perp}$  charge would be even more important than for Al(001) and compatible with the outward experimental relaxation obtained for the former surface. On the other hand, for the less compact Al(110) surface, the effect is expected to be less important, ending in the experimentally observed inward relaxation of this surface. A quite similar description was given by Fall *et al.* in Ref. 29 from pseudopotential calculations, performed to explain another anomalous behavior of Al surfaces: the trends

TABLE V. Electronic partial charges (in  $e^-$ ) within the corresponding atomic spheres ( $R_{MT}=2.65$  bohr) of  $3p_{||}=(3p_x+3p_y)/2$  and  $3p_{\perp}=3p_z$  character for the unrelaxed and relaxed Al(001) surfaces using  $23L$  slabs.

Atom	$p_{\perp}$		$p_{  }$	
	Unrelaxed	Relaxed	Unrelaxed	Relaxed
Surface	0.250	0.245	0.296	0.293
S-1	0.335	0.330	0.332	0.329
S-2	0.328	0.327	0.331	0.330
S-3	0.333	0.334	0.330	0.330
S-4	0.334	0.335	0.332	0.333
S-11 (bulk)	0.331	0.331	0.331	0.331

in the work function anisotropy for the Al(110), Al(001), and Al(111) surfaces. They have also addressed the inward or outward relaxation behavior of these surfaces, arguing that outward relaxations can be understood in terms of the strengthening (weakening) of the atomlike  $p_{||}$  ( $p_{\perp}$ ) surface orbitals resulting in their different occupations compared with the bulk situation. However, no occupations were reported by these authors. Thus, we conclude that the important parameter is the population imbalance between the  $p_{||}$  and  $p_{\perp}$  surface orbitals as well as a transfer from  $p$  to  $s$  states as compared to the bulk.

Numerical experiments were carried out by Fall *et al.*<sup>29</sup> in order to explore the relaxation behavior as a function of the  $p$  valence electron population of Al (virtual) atoms. They recover the *normal* inward relaxations for Al(001) and Al(111) surfaces when no partially filled  $p$  bands exist anymore. In fcc simple metals, the Fermi level is found among the  $p$  bands (as well as  $s$  bands), but the  $p$  character is somehow stronger for the Al metal than for other materials that exhibit a normal relaxation. Then, the anomalous outward relaxation of Al(001) and Al(111) would be just a manifestation of this strong  $p$  character that plays an important role controlling the surface properties. The face-dependent filling of the  $p$  states at the Al surface would be responsible for the outward surface interlayer relaxation.

#### 4. Friedel oscillations

The preceding analysis concerns the main surface relaxation; however, it does not explain the presence of multilayer relaxations. One possibility would be the presence of Friedel oscillations. Figure 3(a) shows that, besides the rearrangement of charge within the surface interlayer, there are charge oscillations between successive atomic layers when going from the surface to the bulk. Compared to the bulk densities within the first interlayer, an important charge depletion is found, while within the second layer, a charge accumulation between atoms is observed. Inside the second interlayer, Fig. 3(a) shows zones with more and others with less charge density than in the bulk, whereas in the third and fourth interlayers, a slight accumulation of charge is observed. These charge oscillations, obtained when electrons try to screen the formed surface (but without considering any atomic relax-

ations yet), are nothing else than Friedel oscillations<sup>47</sup> for the Al(001) surface. Presented in a spatially resolved (nonaveraged) way, we will call them distributed Friedel oscillations. It is interesting to note that the distributed Friedel oscillations for the Al(001) surface, along vertical lines joining atoms in Fig. 3(a), have an almost layer by layer oscillation pattern and not the multilayer relaxation pattern of Fig. 1. The charge density redistribution of Fig. 3(a) is responsible for the total forces of the unrelaxed slab given in Table IV. We now explore the effect of atomic relaxations analyzing Fig. 3(b), where the electron density difference between the relaxed minus unrelaxed slabs is shown. An interlayer by interlayer analysis of this figure reveals that the first and second interlayers have less charge density than the unrelaxed case. The third interlayer presents zones with more or less charge density than in the unrelaxed case, but for the fourth interlayer more charge density is found. As may be expected, the charge density redistribution shown in Fig. 3(b) has almost the same oscillating pattern than the multilayer relaxations. The charge density redistribution of Fig. 3(b) is compatible with the fact that the first three interlayers relax outward (with bigger values for the first two and an almost zero value for the third one, see Table II), while the fourth interlayer relaxes inward with a non-negligible relaxation value. The relaxed slab minus bulk charge density difference given in Fig. 3(c) reveals an oscillatory behavior different from the almost layer by layer oscillation of Fig. 3(a) and the several interlayers by cycle of Fig. 3(b). The surface interlayer shows in Fig. 3(c) a depletion of charge, whereas the fourth interlayer exhibits more charge than the bulk. This is compatible with the outward relaxation of the first interlayer and the inward relaxation of the fourth interlayer. Inside the second and third interlayers, both depleted and accumulated charge density zones exist. Compared to Fig. 3(a), one of the effects of relaxations is to have an almost horizontally flattened zero (thick solid) line that characterizes no changes with respect to the bulk. This allows the interpretation that the relaxed surface is achieved when almost flat pseudointerlayers of more or less charge density (compared to the bulk) are alternatively stacked parallel to the surface. Interestingly, the pseudointerlayers appearing in Fig. 3(c) seem to have an inversion symmetry plane at the third layer, at least for the densities up to two neighboring interlayers.

The relaxation models based on Friedel oscillation ideas<sup>45,48,49</sup> suppose that the oscillations in the electronic charge density at the bulk-truncated surface lead to the oscillatory behavior in the atomic forces, which, in turn, drive the atomic layers to relax in an oscillatory way. In order to apply these ideas to the Al(001) case, we simplify the analysis considering the net charge (ions plus electrons) just on the atomic layers perpendicular to the surface. A careful analysis of Fig. 3(a) reveals a  $---+-$  succession of signs when going from the surface layer (left) to the fifth layer (right), with greater magnitudes for the surface and the second layer. A negative net charge on the latter two layers means an electrostatic repulsion leading to the outward relaxation for the surface interlayer. In the same way, the different net charge between the fourth and fifth layers leads to an inward relaxation. This analysis is compatible with the atomic forces we have obtained in Table IV. However, it is not evident from

these net charges, as is also the case when we have discussed the atomic forces, that the final relaxation will be an expansion for the second and the third interlayers. We may conclude that the Friedel oscillations (considered here only as linear density differences joining the atomic charged layers perpendicular to the surface), as well as the atomic forces, correlate with the final relaxations only for the interlayers that give the maximum amplitude (in absolute value) of Fig. 1. A complete distributed Friedel oscillation consideration is necessary, together with a careful self-consistent force calculation, to put in evidence the complete relaxation pattern shown in Fig. 1. In this way, multilayer relaxations in Al(001) could be understood as the signature of Friedel oscillations that are unable to completely screen the presence of the surface leading to further atomic relaxations up to the final structure. Experience indicates that Friedel-like oscillations may also be present in other quantities than the charge density. In fact, for the relaxed Al(001) surface, they are nicely observed in our multilayer relaxation results shown in Fig. 1.

Finally, are the Friedel oscillations the only mechanism possible to drive multilayer relaxations? In Ref. 51, a phonon based method that predicts the period and the decay constant of multilayer relaxations in a natural way was given. The authors have shown that multilayer relaxations are related to the solutions of zero frequency in the complex phonon structure. As soon as Friedel oscillations are considered as the response the electronic charge density gives to the surface formation, the zero frequency solutions in the complex phonon structure must be considered as the response the bulk phonon structure gives for the same situation. Most probably, both mechanisms complement themselves and are present in multilayer relaxations of real surfaces. In this work, we have addressed the electronic part of the answer. To evaluate the phonon part, an *ab initio* phonon calculation would be made with at least the same numerical precision that we have used in the present work. Such calculations, which are out of the scope of the present work, would be desirable to completely understand the multilayer relaxation phenomena.

### E. Work function

We have calculated the work function  $\Phi = E_{vac} - E_F$  approximating the vacuum energy ( $E_{vac}$ ) as the averaged Coulomb potential in the center of the vacuum region of our slab (38.27 bohr away from the surface atoms).  $E_F$  is the corresponding Fermi energy. We have calculated the work function for both the unrelaxed and relaxed slabs, and our results for the 23 atomic layers +20 vacuum layer slabs are given in Table VI, together with those obtained using other theoretical *ab initio* calculations as well as the experimental results. For the relaxed slab, we have estimated an error bar using the same procedure as for the multilayer relaxations (described in Sec. II)

Our theoretical result for the work function of the relaxed slab is in fairly good agreement with experiment, in between two independent measurements on single crystals of aluminum. It is also in agreement with other *ab initio* calculations. The work function for this surface is not very sensitive to the

TABLE VI. Work function  $\Phi$  (in eV) for the Al(001) surface for unrelaxed and relaxed slabs.

	Unrelaxed slab	Relaxed slab
23L-L/APW+lo-GGA <sup>a</sup>	4.28	4.27±0.01
17L-LAPW-GGA <sup>b</sup>	4.259	4.243
8L-pp-LDA <sup>c</sup>	4.42	4.38±0.03
15L-pp-LDA <sup>d</sup>		4.51±0.03
Expt. <sup>e</sup>		4.20±0.03
Expt. <sup>f</sup>		4.41±0.03
Expt. <sup>g</sup>		4.29 <sup>h</sup>

<sup>a</sup>This work.

<sup>b</sup>Reference 4.

<sup>c</sup>Reference 29.

<sup>d</sup>Reference 30.

<sup>e</sup>Reference 53.

<sup>f</sup>Reference 54.

<sup>g</sup>Reference 55.

<sup>h</sup>For a polycrystalline film.

relaxation. We obtain only a 0.01 eV shift between unrelaxed and relaxed slabs similar to those of other authors. In all cases, the theoretical work function for the unrelaxed slab is found larger than the corresponding value for the relaxed slabs.

### F. Surface energy

To complete the analysis of the Al(001) surface, we present the results of the calculated surface energy  $\sigma$ . The surface energy represents the energy (per surface atom or per unit area) needed to form a surface from the bulk and was obtained using

$$\sigma = \frac{(E_{slab} - NE_{bulk})}{2}, \quad (2)$$

where  $E_{slab}$  is the total energy for the relaxed or unrelaxed slab,  $E_{bulk}$  is the total energy for bulk fcc Al, and  $N$  is the number of layers used in the corresponding slab. The factor 2 in the denominator takes into account the presence of two identical surfaces on the opposite sides of the slab. Strictly speaking, this equation is valid for the  $N \rightarrow \infty$  limit. A slab of  $N=23$  atomic layers is considered to be large enough to approach this limit in practice and to yield a reliable value for the surface energy. There are some discussions in the literature on the way  $E_{bulk}$  should be calculated.<sup>56</sup> The total energy for fcc bulk Al may be obtained from a standard well converged bulk calculation. However, even when the same method for bulk and slab calculations is used and all computational parameters are kept as close as possible, differences in the basis set quality and in the set of implicit parameters (such as the  $k_z$  integration explicitly selected by the number of layers in the slab calculation) result in problems when using Eq. (2) because we need to subtract two big numbers calculated in a different way. Two solutions are possible: (i) to fully converge  $E_{bulk}$  and  $E_{slab}$  with a very accurate method or (ii) to calculate  $E_{bulk}$  directly from slab calcula-

tions, avoiding a direct calculation of the bulk energy from the fcc symmetry. The first alternative gives  $E_{bulk} = (-485.643\,734 \pm 0.000\,001)$  Ry when fcc bulk Al is calculated with exactly the same method-dependent parameters used in the slab calculations, except the  $k$  mesh and the linearization energies that were optimized to a microrydberg convergence. To explore the second alternative, we rewrite Eq. (2) in the form

$$E_{slab} \approx 2\sigma + NE_{bulk}, \quad (3)$$

where the linear dependence of  $E_{slab}$  on  $N$  is put in evidence. For large  $N$ , the linear term will be dominant, and it is possible to extract  $E_{bulk}$  from a linear regression of the slab total energy data versus  $N$  (only for large values of  $N$ ). Care must be taken to calculate the different slabs with exactly the same basis set and parameters. In this way, the  $E_{bulk}$  energy is completely determined from slab calculations. As was shown by Fiorentini and Methfessel,<sup>56</sup> the linear dependence is already dominant for very thin slabs and, accordingly, we have used 19L, 21L, and 23L relaxed slabs to proceed with the calculation of  $E_{bulk}$ . Moreover, the only difference among these slabs is the number of atomic layers. All other structural as well as method-dependent parameters are exactly the same. The Al bulk energy calculated in this way is  $E_{bulk} = (-485.643\,77 \pm 0.000\,07)$  Ry. The error value corresponds to the error in the slope given by the regression method. Comparing this  $E_{bulk}$  value with that obtained from the bulk calculation, we observe a difference of only 36  $\mu$ Ry. It is interesting to compare this difference with the 700  $\mu$ Ry difference obtained for the Pt(100) case study by Fiorentini and Methfessel<sup>56</sup> using the full-potential linear muffin-tin orbital (FP-LMTO) method and used to argue in favor of the second alternative as the correct method to calculate the bulk energy. From our results, we may state that both alternative calculations tend to converge with high precision to the same value as long as not only the same method, but also the same parameters in highly converged calculations (except the  $k$  mesh and the linearization energies) and sufficiently big slabs in the regression procedure, are used. Da Silva,<sup>4</sup> using a film-LAPW-based method, found similar inconsistencies for the bulk energy of Al calculated in the two ways. In this case, however, the author himself stated that the inconsistencies must be attributed to the different qualities of basis sets used for the bulk and slab calculations. As a conclusion, we have found that there are no substantial differences in the Al bulk energy obtained from bulk calculations or from the slope of the linear regression applied to the slab energy data, as long as highly converged calculations are considered. The convergence of  $E_{bulk}$  from the two types of calculations is achieved at high precision.

We have calculated the surface energy  $\sigma$  corresponding to the unrelaxed and relaxed 23L slabs, using both differently obtained  $E_{bulk}$  energies. As can be seen in Table VII, the use of the different Al bulk energies gives slightly different surface energies. A difference of 6 meV/surface atom is found, which is, however, still smaller than the estimated error bars.

Our calculated surface energy is lower than the experimental value obtained from thermodynamical measurements

and extrapolated to 0 K (0.584 eV/surface atom). However, it must be noted that the experimental value is obtained for a general Al surface and not for the specific Al(001) surface. The agreement among the theoretical values is around 15%, and the results strongly depend on how  $E_{bulk}$  is calculated and on the number of atomic layers included in the slabs. The surface energy decreases in all calculations from the unrelaxed slab to the relaxed one due to the energy gain in the multilayer relaxations. However, the energy gain due to relaxation is very small and the *relaxation energy* (difference between the  $E_{slab}$  from the unrelaxed and relaxed slabs) is just 1 meV/surface atom for the Al(001) surface.

#### IV. CONCLUSIONS

Theoretical calculations of multilayer relaxations for the pure Al(001) surface were performed using the full-potential L/APW+lo method using a slab of 23 atomic layers plus 20 vacuum layers. Special care was taken to obtain reliable results which are converged with respect to the different structural as well as method-dependent parameters. Error bars were given for all calculated properties as an indication of the precision of our results. In this way, we have obtained an outward relaxation for the surface interlayer of  $(1.51 \pm 0.06)\%$ , which compares fairly well with the last experimental LEED results. We have also found that relaxations are not limited to the surface interlayer but propagate deep into the material, giving a damped oscillatory relaxation wave pattern, whose oscillations take several interlayers, instead of the common layer by layer oscillation pattern. Our results predict an expansion of the first three interlayers, a contraction of the following four interlayers, again an expansion of the following layers, and so on, with a damped amplitude approaching zero at the middle of the slab. The biggest amplitude of expansion is obtained for the surface layer with the above cited value. The biggest contraction is obtained for the interlayer between layers 4 and 5, with a value of  $(-0.40 \pm 0.01)\%$ . Our results suggest that a new experimental determination of the Al(001) multilayer relaxations should be performed, which should include the possibility of  $d_{4,5}$  interlayer relaxation in the model used to fit the  $I(V)$  curves of LEED experiments.

A careful analysis of the *ab initio* calculated forces on atoms at each layer for the unrelaxed slab suggests that we must discard the commonly supposed correlation between the forces obtained for the unrelaxed slab and the final results after relaxations. Instead, our results show that the forces for the unrelaxed slab correlated only with the absolute maxima of the damped relaxed wave. For the layers corresponding to these maximum interlayer distances, the forces of adjacent layers for the unrelaxed slab are in opposite direction, explaining in a natural way the expansion or contraction. On the other hand, all other layers have forces in the same direction, and it is not evident if the final result will be an expansion or a contraction. This raises the importance of a careful full structural relaxation until the remaining forces are sufficiently small.

In order to understand the calculated multilayer relaxations, we have performed an exhaustive analysis of the

TABLE VII. Surface energy  $\sigma$  (in eV/surface atom) for the Al(001) surface from various theoretical *ab-initio* methods and experiment.

	Unrelaxed slab	Relaxed slab
23L-L/APW+lo-GGA <sup>a</sup>	0.489	0.488±0.007
23L-L/APW+lo-GGA <sup>b</sup>	0.495	0.494±0.014
17L-LAPW-GGA <sup>c</sup>	0.486	0.484
9L-pp-LDA <sup>d</sup>	0.585	0.551
FCD-LMTO-GGA <sup>e</sup>	0.689	
pp-GGA <sup>f</sup>		0.582
15L-pp-GGA <sup>g</sup>		0.54
Expt. <sup>h</sup>	0.584	

<sup>a</sup>This work, using  $E_{bulk}$  from bulk fcc calculations.

<sup>b</sup>This work, using  $E_{bulk}$  from slabs calculations.

<sup>c</sup>Reference 4.

<sup>d</sup>Reference 28.

<sup>e</sup>Reference 57.

<sup>f</sup>Reference 58.

<sup>g</sup>Reference 30.

<sup>h</sup>Reference 59. No specific surface plane was given.

charge density for both the unrelaxed and relaxed slabs as well as for bulk aluminum. The comparison was made for the surface plane and the (100) plane perpendicular to the surface. The found extra charge between nearest neighbor atoms of the surface plane and the depletion of charge between surface atoms and its nearest neighbors in the second layer come from an anisotropic occupation of the Al 3*p* orbitals, where the  $p_{\parallel}$  states are energetically more favorable than the  $p_{\perp}$  states. In this way, the outward relaxation for the topmost interlayer can be understood in terms of the imbalance of the  $p_{\parallel}$  and  $p_{\perp}$  surface orbitals, which is a significant effect in Al (compared to other simple metals) due to the strong *p* character of states at the Fermi energy. This imbalance correlates with the compactness of the surface and is expected to be more (less) important for Al(111) [Al(110)] than for the Al(001) surface. Outward relaxations of Al(001) and Al(111) are related to this population imbalance and to the strong character of *p* states of Al at the Fermi energy. Distributed Friedel oscillations were identified in the charge density difference between the unrelaxed slab and the bulk.

A simple electrostatic layer model correlates with the forces obtained for the unrelaxed slab and lets us understand both the maximum outward (surface layer) and the maximum inward (between the fourth and fifth layers) relaxations in the damped oscillatory relaxation pattern. This correlation is valid only for the above mentioned interlayers, and a complete consideration of the distributed Friedel oscillations as well as self-consistent force calculations are needed to completely describe the relaxation pattern. In this way, Friedel oscillations may be considered as responsible for the electronic driven contribution to the multilayer relaxations. Phonon driven contributions could also be present, but would need to be calculated with at least the same numerical precision that we have used in the present work.

Finally, we have presented results for the work function and surface energy for the unrelaxed and relaxed slabs. In both cases, only a small dependence of these magnitudes on the relaxation was found. The calculated values for the work function and the surface energy agree reasonably well with the experimental results as well as other theoretical *ab initio* results. To evaluate the surface energy, special care was taken to calculate the Al bulk energy from the fcc symmetry as well as from slab calculations. We have obtained almost the same bulk energy by performing high precision calculations using well converged and identical method-dependent parameters (except *k* mesh and linearization energies) for the fcc bulk as well as the 19*L*, 21*L*, and 23*L* slabs. Such high precision calculations could produce quite similar surface energies and could estimate a theoretical error bar for the surface energy.

As a final conclusion, the state of the art *ab initio* calculation performed for the Al(001) surface is a reliable tool to investigate subtle effects such as the deep relaxation pattern predicted for this surface. These results should motivate further experimental multilayer relaxation studies for this surface.

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