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Anomaly in the anisotropy of the aluminum work function

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Ab initio calculations combined with a recently developed macroscopic-averaging technique have been used to examine the anisotropy of the aluminum work function. Our results indicate that the Al(111) work function is substantially lower than the Al(100) work function, and slightly below the Al(110) work function. This is in contrast to other fcc metals, for which a $(110)\rightarrow(100)\rightarrow(111)$ increasing trend is observed experimentally and predicted by Smoluchowski's rule. We show that the aluminum work-function anomaly, which is in agreement with experiment, is due to the increased p-atomic-like character of the density of states at the Fermi energy, as compared to most other fcc metals. [S0163-1829(98)50436-5]

The work-function anisotropy of elemental metals has been the focus of many early theoretical studies.[1] Ultrahigh vacuum and epitaxial growth techniques, such as molecular-beam epitaxy, have recently allowed unprecedented control of the quality of crystal surfaces, so that it is now possible to determine the dependence of the work function on the surface crystallographic orientation with a high degree of accuracy. Renewed interest has also been stimulated by the possibility of obtaining images of the local work function at metal surfaces by scanning tunneling microscopy.[2]

Most fcc metals in which the work function anisotropy has been measured,[3,4] such as Ni, Cu, or Ag, show the same $(110)\rightarrow(100)\rightarrow(111)$ trend of increasing work function with varying crystallographic orientation. This ordering is consistent with the Smoluchowski model,[5] which attributes the work function anisotropy to the smoothing of the electron density at the surface. The resulting work functions increase with the atomic packing of the surface, as found experimentally for most metals. The work function of aluminum exhibits a different trend, namely, it increases in going from the (111) to the (110) and to the (100) surface.[6] This trend violates Smoluchowski's rule, and can be explained neither by the linear theory of Lang and Kohn,[7] which includes discrete-lattice corrections to a jellium surface, nor by an extension including higher-order effects.[8] Moreover, while most atomic surfaces of elemental metals show inward relaxation, as predicted by Finnis and Heine's electrostatic model[9] based on Smoluchowski smoothing, the top atomic layers of the Al(100) and Al(111) surfaces relax outward.[10,11] These trends are surprising, since a simple sp metal such as Al would be expected to be more closely approximated by a jellium than transition metals such as Ni, Cu, or Ag.

In this paper we explain the anomalous behavior of the surfaces of aluminum based on an *ab initio* approach. In particular, we have identified a mechanism specific to open p-shell metals that induces work-function anisotropies that can reverse the trend expected from Smoluchowski's rule. This mechanism also explains the anomalous outward relaxation of the Al(111) and Al(100) surfaces.

Our *ab initio* calculations are performed within density-functional theory in the local-density approximation using the Ceperley-Alder exchange-correlation functional.[12] We use Troullier-Martins pseudopotentials[13] in the Kleinman-Bylander nonlocal form.[14] A set of Monkhorst-Pack[15] special points are used for the Brillouin-zone integrations, together with a Gaussian broadening scheme,[16] with a full width at half maximum of 0.01 Ry, to position the Fermi level. A plane-wave basis is used to expand the electronic wave functions.

For each surface orientation i, the work function W_i may be written as $W_i = D_i - E_F$, where E_F is the Fermi energy measured with respect to the Al average electrostatic potential, and D_i is the electrostatic potential step at the surface, which contains all the orientation dependence. The quantity E_F is calculated in a bulk Al crystal to avoid quantum size effects,[17] using a cutoff of 36 Ry and 570 reduced k points. The surface dipoles D_i are obtained from self-consistent calculations of the charge density in supercells containing a metallic slab surrounded by vacuum regions. A macroscopic averaging technique, previously employed in the study of band offsets at semiconductor heterojunctions,[18] is used to determine precisely the potential step D_i between the crystal and the vacuum regions. Surface ionic relaxations have been studied by allowing the top two or three layers of each slab to move to their equilibrium positions, thereby minimizing the Hellmann-Feynman forces. The central layers are kept fixed at the bulk interplane distance in order to retain the crystal periodicity over a small region and perform the macroscopic average. The calculations for the (111) surface were performed using a $9+6$ supercell (9 planes of Al, 6 equivalent planes of vacuum) and 36 k points in the irreducible Brillouin zone. The corresponding values used for the (100) surface are an $8+6$ supercell and 45 k points, and for the (110) surface an $8+8$ supercell and 48 k points. These slabs are thick enough to minimize quantum size effects on surface dipoles and atomic relaxation.[17,19] A cutoff of 16 Ry was used for the plane-wave expansion of the electronic wave functions in the supercells. With these parameters, the numerical uncertainty on the values of the work functions is estimated to be ~ 0.03 eV.

In Table I, our results for the work functions of the relaxed and unrelaxed surfaces are compared with experiments.[6] The theoretical values agree to within 0.04 eV with experiment and successfully reproduce the anomalous

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TABLE I. Theoretical values of the aluminum work function, in eV, for the three principal surface orientations, as obtained with (W_{relax}^{calc}) and without (W_{unrel}^{calc}) surface relaxation. The theoretical values are compared with the experimental data (W^{exp}) of Ref. 6. Below, the top three interplane surface relaxations (Δd^{calc}), in percent, are compared with the experimental data (Δd^{exp}) of Refs. 10, 11, and 21 for the (111), (100), and (110) surfaces, respectively. Where no data is given, the interplane variations were found to be negligible.

	(111)	(100)	(110)
W_{relax}^{calc}	4.25	4.38	4.30
W_{unrel}^{calc}	4.23	4.42	4.29
W^{exp}	4.24 ± 0.03	4.41 ± 0.02	4.28 ± 0.02
Δd_{12}^{calc}	$+0.8$	$+0.9$	-8.5
Δd_{23}^{calc}	$+0.5$	$+0.4$	$+4.8$
Δd_{34}^{calc}			-2.0
Δd_{12}^{exp}	$+1.7\pm0.3$	$+1.8$	-8.6 ± 0.8
Δd_{23}^{exp}	$+0.5\pm0.7$		$+5.0\pm1.1$
Δd_{34}^{exp}			-1.6 ± 1.2

(111)→(110)→(100) surface ordering. The effect of the surface multilayer relaxations on the work functions is shown to be negligible for all orientations, when compared with the numerical accuracy. This indicates that the effective charges of the ions in the surface layers vanish, an observation consistent with the sum rule recently derived for effective charges at crystal surfaces.[20]

For the relaxed surfaces, the variations of the top interplane distances are displayed in Table I and are compared with experimental low-energy electron diffraction data.[10,11,21] The small outward relaxations of the Al(111) and Al(100) surfaces are well reproduced, as well as the damped oscillatory behavior of the Al(110) multilayer relaxations. Finnis and Heine's electrostatic model based on Smoluchowski smoothing predicts[9] inward relaxations of the top layers, which increase when the atomic packing of the surface decreases. Although we find outward relaxations for the Al(100) and Al(111) surfaces, the strong contraction of the (110) surface layer is in qualitative agreement with this model [which predicts a contraction of −16% for the (110) top interlayer distance[9]].

Having shown that surface relaxations produce negligible modifications of the work functions, our discussion and interpretations of the work-function trends will be focused on unrelaxed surfaces. In order to model the surface electronic charge density, the crystal surface may be approximated, as a first step, by a superposition of atomic charge densities or of bulk Wigner-Seitz unit cells. Neither of these possibilities induces any orientation dependence in the work-function. They may therefore be taken as convenient reference electron surface distributions to understand the mechanism behind the Al work function anisotropy. In Fig. 1, we have plotted the electronic charge density of the self-consistent Al(100) surface and compared it with the superposition of atomic charges as well as the surface built from bulk Wigner-Seitz unit cells. As for most metals, the atomic charges model heavily overestimates the work function,[22] yielding $W_{at}=7.59$ eV, to be compared with the self-consistent result $W_{100}=4.42$ eV, whereas the Wigner-Seitz model strongly underestimates it with a value of $W_{WS}=0.33$ eV. The self-consistent charge is seen to follow closely the Wigner-Seitz density inside the crystal, but to approach the atomic distribution in the vacuum region. Around the surface ions, the contracted wave functions of the bulk crystal tend to relax back to their atomic dimension in the direction perpendicular to the surface, and the related charge transfer increases the surface dipole.

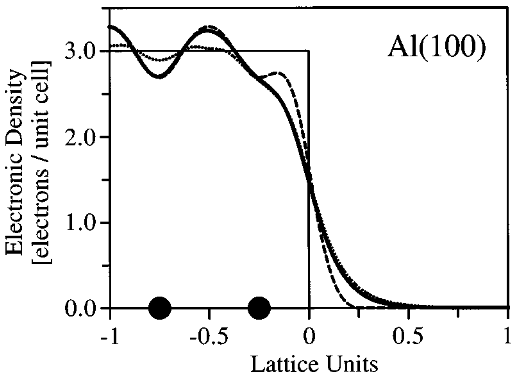

FIG. 1. Planar average of the electronic charge density for the Al(100) surface, as a function of the distance to the surface. Solid line: self-consistent charge density; dashed line: surface formed by repeating the charge density of bulk Wigner-Seitz unit cells; dotted line: superposition of atomic charge densities. The rectangle gives the macroscopic ionic charge density. The black disks indicate the atomic planes.

In the case of an open p-shell metal such as Al, this suggests the existence of an important asymmetry between the directional atomiclike p orbitals of the surface ions. The $p_{\parallel}$ states, parallel to the surface, can be expected to be occupied differently from the $p_{\perp}$ states, perpendicular to it. The $p_{\parallel}$ states are energetically favorable, when compared to the $p_{\perp}$ orbital that extends into the vacuum and regions of higher potential. In Fig. 2, we have plotted the difference between the electronic density in the surface plane of Al and the den-

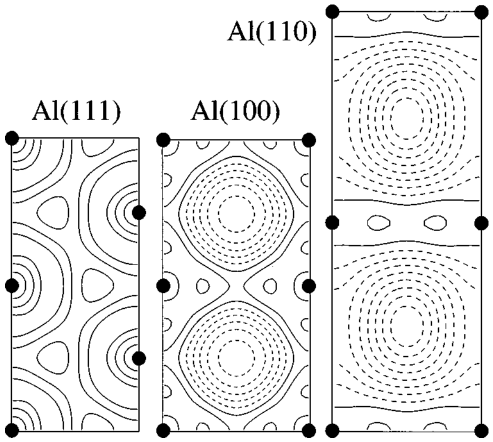

FIG. 2. Contour plots of the electronic charge density difference between the exact self-consistent charge in the aluminum surface plane and the corresponding plane in a bulk Al crystal. The contours are equally spaced [by 0.02, 0.05, and 0.2 (e^{-}/unit cell) for the (111), (100), and (110) orientations, respectively]. The dashed lines correspond to negative values and the black disks to the positions of the ions.

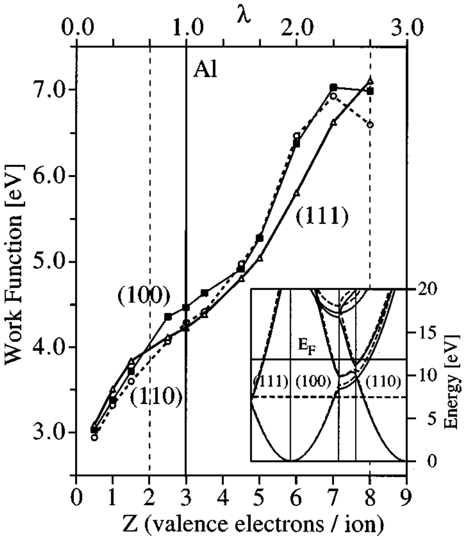

FIG. 3. Work functions of the virtual Al_Z crystals for the three principal surface orientations, as a function of the valence charge Z (lower axis) and the Al pseudopotential scaling factor λ (upper axis), as detailed in the text. (111): triangles; (110): squares; (100): circles. The solid vertical line shows the position corresponding to the real Al crystal. Vertical dashed lines delimit the filling of different orbital states. The inset shows the band structure of Al (continuous lines) and $\mathrm{Al}_{1.5}$ (dashed lines), along selected directions in the Brillouin zone. The energy zero is set at the band minimum in both cases. The Fermi level is situated at 11.43 and 7.47 eV in Al and $\mathrm{Al}_{1.5}$, respectively (horizontal lines).

sity in a corresponding bulk plane. Despite the supplementary freedom allowed by the possible spreading of the valence electrons into the vacuum, the surface plane in the Al(111) direction shows an all-over increase in density with respect to the bulk situation. In the Al(100) and Al(110) directions, the density is similarly increased along the bonds between nearest neighbors. Compared with the bulk situation, the extra density in the $p_\parallel$ states, which increases with the surface atomic packing, results in a lower occupation of the $p_\perp$ orbitals, and yields a surface dipole that *decreases* with increasing surface packing.

This view is supported by the following numerical experiment, in which we have sought to modify the number of valence electrons associated with each Al ion. We have defined a series of virtual atoms Al_Z, with varying valence Z, by using pseudopotentials linearly scaled from that of aluminum. Since Al has three valence electrons, to retain charge neutrality Al_Z is associated with $Z=3\lambda$ electrons, where λ is the pseudopotential scaling factor. We then computed self-consistently the work functions of the corresponding Al_Z crystals, i.e., a series of crystals composed of Al_Z pseudoatoms on an Al fcc lattice.[23] The results for the three principal directions are plotted in Fig. 3 as a function of the number of electrons per ion (and of λ). It is seen that for low values of the density, the ordering of the work functions follows the Smoluchowski prediction and increases from (110) to (100) and to (111). However, as the number of valence electrons per ion is increased above two, the trend of the (111) surface changes and it crosses below the other directions. As the density rises further, a number of other crossings are observed.

As shown in Fig. 3, the Smoluchowski rule correctly describes the work-function anisotropy when the only occupied levels around each ion are s states. The inset in Fig. 3 shows the bulk band structures of Al and $\mathrm{Al}_{1.5}$ along the three directions of interest. We observe that below the Fermi level of Al the band structure depends weakly on the value of the electronic density. As λ changes, only the position of the Fermi level is modified significantly to accommodate the different number of electrons in the crystal. For low values of the electronic density, in the Smoluchowski regime of the work function, the Fermi level is positioned on the nearly parabolic isotropic s band. The first sign of a change in the trend of the work function occurs for the Al(111) face when the states at the bottom of the p band begin to be filled, near the edge of the Brillouin zone in the (111) direction. The electronic wave functions of the surface are indeed expected to derive from bulk states with similar energies in the semi-infinite system. As the electronic density increases, the anisotropic p bands are increasingly filled and the work function becomes highly anisotropic.

We thus suggest that it is the face-dependent filling of the atomiclike p states at the surface that is responsible for the work-function anisotropy in Al. The occupation of the $p_\parallel$ states is affected by the position of the ionic neighbors, and hence by the surface orientation. A modification of the number of valence electrons in $p_\parallel$ states induces a change in the filling of the $p_\perp$ states and therefore of the surface dipole. The (111) surface has the highest number of nearest neighbors in the surface plane and the $p_\parallel$ states are highly favored. This results in fewer electrons in the $p_\perp$ orbitals and leads to a lower surface dipole compared to other orientations. The Al(111) work function therefore dips below the other two orientations at an early stage when the electronic density is artificially raised. The second most dense surface is (100) and, as seen in Fig. 3, it is the second direction to dip below the (110) direction when the p states are filled. The (110) direction then exhibits the largest work function. At this point Smoluchowski's ordering has been reversed. When the p states are nearly completely occupied, the work functions show further crossings, in reverse order to which they first appeared. For eight electrons per ion, the p states are fully occupied and the contribution of the p orbital filling to the anisotropy disappears. The work functions are then seen to be ordered similarly to the low-density situation.

The anomalous outward relaxation of the Al(111) and Al(100) top layers can be similarly understood in terms of the weakening/strengthening of the atomiclike $p_\perp/p_\parallel$ surface orbitals resulting from their different occupation with respect to the bulk situation. We have examined the surface relaxation of an $\mathrm{Al}_{1.5}$ crystal, which contains no filled p bands, and the anomalous outward relaxations are found to disappear in this case. Moreover, for Al_8, in which the p bands are completely filled, the (100) and (111) surfaces show standard inward relaxation.[24]

In this light, the ordering of the work functions in Al is seen to arise from the interplay of two trends. At low electron densities, Smoluchowski smoothing is seen to describe correctly the trend of the surface-dependent dipoles. When p bands are filled, the trend changes and depends on the exact number of valence electrons per ion. The exceptional nature of Al among fcc metals results from its Fermi level positioned among p bands. In other fcc metals such as Cu, Ag, or Ni, the electronic orbitals controlling the surface properties have a dominant s character; the very localized d orbitals are not expected to contribute strongly to the anisotropy. These elements all show the same standard work-function anisotropy.[3,4] We have also examined the anisotropy of a bcc metal, Na, which has an isotropic band structure with one s electron. In this case, the most dense Na(110) surface has a higher work function (3.00 eV) than Na(100) and Na(111) (2.80 and 2.79 eV, respectively), consistent with Smoluchowski's rule. Finally, other elemental metals with a larger valence Z than Al tend to lose their cubic structure, and the work function is then influenced by the macroscopic anisotropy of the crystal structure.

In conclusion, we have explained the Al work-function anomaly by means of a microscopic *ab initio* approach. The anisotropy trend of the work function in Al can be explained by a charge transfer from the atomiclike p orbitals of the surface ions perpendicular to the surface plane to those parallel to the surface, when compared to the bulk charge density. The anomalous outward relaxation of the Al(100) and Al(111) top layers can similarly be understood in terms of a charge transfer among surface p orbitals. The exceptional nature of the Al work function and surface atomic relaxation, when compared to other fcc metals, results from a dominant p-atomic-like character of the density of states near the Fermi energy.

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[24] The relaxations at the surfaces of the virtual crystals are determined at their respective theoretical lattice constants.