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Ab initio study of γ-Al₂O₃ surfaces

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Starting from the theoretical prediction of the γ-Al₂O₃ structure using density-functional theory in the generalized gradient approximation, we have studied the (1 1 1), (0 0 1), (1 1 0), and (1 5 0) surfaces. The surface energies and their corresponding structures are computed and compared with predictions for (0 0 0 1) α-Al₂O₃ and available experimental results for γ-alumina surfaces. (1 1 1) and (0 0 1) surfaces are predicted to be equally stable, but to show quite different structure and reactivity. Whereas a low coverage of highly reactive trigonal Al occurs on (1 1 1), (0 0 1) exhibits a more dense plane of both five-coordinate and tetrahedral Al. Microfaceting of a (1 1 0) surface into a (1 1 1)-like planes is also observed. The implications for the structure of ultrathin dielectric films and for the surfaces of disordered transition aluminas are discussed.

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I. INTRODUCTION

Considering the technological importance of alumina (Al₂O₃), it is surprising that no reliable atomic-scale model exists for the surface structure of the amorphous phase or of the transition aluminas. This is partly due to experimental difficulties in preparing uniform surfaces, free of impurities, but also due to the structural complexity of the bulk phases and the need for high-quality theoretical treatments. Developing and understanding structural models for the surfaces of the transition alumina γ-Al₂O₃ is the aim of this work.

Alumina is a widely used ceramic and many applications depend on its surface properties, e.g., as ultra-hard coatings, microporous catalysts, and in electroluminescent flat-screen displays. As a modestly high-permittivity material with a wide bad gap and abrupt interface to Si, thin-film Al₂O₃ is already being used in read/write heads and node dynamic random access memory (DRAM) and is a candidate gate dielectric for next-generation transistors. Integration into these technologies places stringent demands on processing and performance of the active thin film, and so requires an understanding of the film surface.

Alumina can be prepared in a variety of solid polymorphs. Corundum or sapphire, α-Al₂O₃, is the most stable. Its bulk structure may be described as a hcp O sublattice with two-thirds of the octahedral interstices filled by Al in close packed and where Al is distributed between four- and six-coordinated sites. Alumina is a block metal oxide with a wide bad gap (ca. 9 eV) and it does not readily form suboxides (ratio Al:O<2:3). The occurrence of O vacancies is not fully understood: in a recent theoretical study on both bulk and (0 0 0 1) α-Al₂O₃, the authors have computed O-vacancy formation energies of the order of 10 eV both in the bulk and at the surface. On the other hand, experimental results show that annealing of alumina in ultra-high vacuum yields metallic Al overlayers rather than a suboxide. In any case, we are interested in gamma-alumina samples that have been prepared under oxygen-rich conditions, e.g., by dehydration of hydroxide or by chemical vapor deposition. In the latter case, alumina films of stoichiometry Al:O=2:3 are deposited, even for 1 nm films on HF-treated Si. We therefore restrict our study to such stoichiometric slabs/surfaces.

Much recent experimental and theoretical work has addressed the controversial question of the bulk structure of γ-Al₂O₃, as summarized in Refs. 11 and 19. γ-Al₂O₃ is a defective spinel and so the main point of contention is the cation vacancy distribution. In a hypothetical Al₂O₄ spinel, two-thirds of Al are octahedrally coordinated to O (O₆) and one-third tetrahedral (O₄), the latter in pairs that face-share vacant Al octahedra (V(O)). More cation vacancies (V(O) or V(T)) must therefore be introduced into this spinel to reduce the Al concentration by one-ninth and produce the sesquioxide stoichiometry. Of the N octahedral and 2N tetrahedral interstices of the fcc sublattice of N oxide anions, only 2N/3
should be occupied by Al cations and this can be achieved in about 1010 distinct ways. Most authors agree that $V_{O_h}$ are favored, but that there is a statistical distribution of up to 30% $V_{T_d}$ in a room-temperature sample of $\gamma-Al_2O_3$.21,22

Much of the catalytic activity of alumina surfaces can be traced to the electronic structure. Coordination unsaturated Al ions at the surface show empty surface states, typically within the bulk band gap and localized primarily on Al. The closer these states lie to the Fermi level, the more reactive they are. A Fourier transform-infrared (FT-IR) study of partially dehydroxylated $\gamma-Al_2O_3$ with adsorbed pyridine shows three types of Lewis acid site on the surface, assigned to three-, four-, and five-coordinate Al.23 On the other hand, solid-state NMR indicates a variety of surface Al, none of which can be assigned as three coordinate (trigonal).24

Considering theoretical approaches to modeling alumina, rigid pair potentials are found to be inadequate for the bulk, requiring charge transfer or quadrupolar corrections.25 Studies using the more reliable but computationally demanding density-functional theory (DFT) have concentrated on the $(0 0 1)$ and $(1 1 0)$ surfaces of $\gamma-Al_2O_3$, in implementations that model the surface as a periodic slab or as a cluster.29 However, some of these suffer from deficiencies in modeling $\gamma-Al_2O_3$ (nonstoichiometry, absence of vacancies or high H concentration) or in adequately representing a surface (insufficient slab area or thickness, frozen atoms). More relevant for the current work on close-packed O surfaces is a periodic DFT study of the hcp-based $\kappa-Al_2O_3$ and its close-packed $(0 0 1)$-like surfaces; significant relaxation of surface Al is discussed in terms of subsurface tetrahedral Al and vacancies.

II. COMPUTATIONAL METHOD

First-principles calculations give a reliable description of materials and their surfaces at the atomic scale and we apply this method to alumina using the VASP code.31,32 In order to compute the ground-state electronic wave function within periodic boundary conditions, a plane-wave (PW) basis set and Vanderbilt ultrasoft pseudopotentials (USPP)33,34 are used. Electron correlation is accounted for in an approximate way by use of DFT in the generalized gradient approximation (GGA) as parametrized by Perdew and Wang (GGA-II or PW91).35

In order to obtain self-consistent valence-electron wave functions by minimizing the Kohn-Sham total energy functional, we use the residual minimization scheme (RMM-DIIS).34 Convergence with respect to $k$ points of less than 0.02 eV/Al$_2$O$_3$ is achieved with a suitable Monkhorst-Pack mesh and a PW kinetic energy cutoff of 396 eV. A Fermi-level smearing of 0.1 eV is used for improving the total-energy convergence. Finally, the ions are allowed to relax until the forces are less than 0.03 eV/Å. In order to compare our results we perform several computations using the CASTEP code within the GGA-II approach and Vanderbilt USPP with a $(4 \times 4 \times 1)$ Monkhorst-Pack mesh and a kinetic cutoff energy of 390 eV; within these parameters we converge the total energy to less than 0.02 eV/Al$_2$O$_3$. The ionic relaxation is performed until the root-mean-square forces are less than 0.03 eV/Å. It is important to stress the fact that we use GGA-generated USPP within VASP computations while in CASTEP we use local-density approximation (LDA)-generated USPP. It is worthwhile mentioning that although LDA and GGA yield similar results, GGA is better in describing the structure and energetics of alumina polymorphs.11

In order to get a more fundamental understanding about the bonding in both bulk and surfaces of $\gamma-Al_2O_3$, Mulliken population analysis has been performed. It is well known that the PW basis set is deficient in quantifying local atomic properties. We have therefore used the technique suggested by Sánchez-Portal et al.39,40 for projecting the PW onto a basis that is a linear combination of atomic orbitals (LCAO). The quality of this technique is measured by the so-called spilling parameter that in our case is less than 0.008.

Finally, in order to check the robustness of selected surfaces, we performed microcanonical molecular dynamics (MD) using VASP. The total free energy is conserved and the velocity-Verlet algorithm for integrating the Newton’s equations is used. Throughout these simulations, we allow electronic relaxation in order to keep the electrons near the Born-Oppenheimer surface. The ionic time step was 2 fs and the whole simulations lasted 0.3 ps at an approximated temperature of 700 K, appropriate for the conversion of hydroxides to $\gamma$- or $\eta-Al_2O_3$ (500–800 K) and much lower than that required to form $\theta-$ or $\alpha-Al_2O_3$ (1100 K, 1300 K).13 The supercell is held fixed throughout the MD run, which also prevents any unwanted decomposition of bulk $\gamma-Al_2O_3$ within the slab. We note that the computed mean square displacements (MSD) values are only a coarse approximation, due to the short MD time carried out.

III. STRUCTURAL AND ELECTRONIC PROPERTIES OF BULK $\gamma-Al_2O_3$

To validate our method and serve as a reference, we computed bulk corundum, $\alpha-Al_2O_3$. The hexagonal unit cell contains 30 ions, arranged in six $(0 0 0 1)$ Al$_2$O$_3$ layers. Al cations in local $D_{3d}$ symmetry occupy two-thirds of the octahedral sites between alternating layers of hcp O anions. The geometry of both cell and ions was optimized as detailed above to yield $a=4.751$ Å, $c/a=2.757$, which agrees with experiment ($a=4.751$ Å, $c/a=2.730$) within the accuracy expected for GGA. This corresponds to a $(0 0 0 1)$ spacing of 2.18 Å between O layers.

As mentioned in the introduction, $\gamma-Al_2O_3$ has a defective spinel structure and the smallest stoichiometric cell is built up by stacking three MgAl$_2$O$_4$ primitive cells (space group $Fd\bar{3}m$), replacing all the Mg with Al and finally extracting two Al atoms to give vacancies. Since this aluminium sublattice possesses 6 $T_d$ and 12 $O_h$ sites per cell, there are then 17 possible nonequivalent configurations for locating 16 atoms on these sites. Of these, four have two Al vacancies on $T_d$ sites ($T_d T_d$), five show both vacancies on $O_h$ sites ($O_h O_h$), and eight are mixed ($O_h T_d$).
stable by 0.14 eV/Al₂O₃ are three structures with mixed va-

cence distributions. From the results, the lowest energy
structure is the O₆O₆(3) system with the maximum spacing
between O₈ vacancies (∼7.45 Å within the cell) in agree-
ment with other DFT studies. This is the model which we
compare our results with a previous work using LDA.

Having recognized those structures, a full relaxation of
shape, volume, and atoms was carried out on each of the
17 structures using a (2 × 2 × 2) k-point mesh (including
the Γ point). The outcome of these relaxations is pictured in
Fig. 1; as expected for a nonisotropic distribution of vacan-
cies, the optimized primitive cells do not correspond to cubic
symmetry in cubic symmetry

In Table I and Fig. 2 we present the structure of the pro-
posed bulk γ-Al₂O₃. The C2/m space group of this structure
points out its deviation from cubic spinel when γ-alumina is
viewed locally. Reoccupying the vacancies allowed us to fit
the structure to cubic symmetry (0.35 Å tolerance), yielding
a cell parameter a=7.99 Å. The average spacing between O
layers is 2.29 Å (along [1 1 1] in the cubic spinel). In the
literature one can find a scatter with respect to the ex-
perimental value of a (in cubic symmetry) from 7.911–7.943 Å. Thus, our result is ∼1% greater than the experi-
mental values and in close agreement with other GGA
results. It is well known that, in general, GGA overesti-
mates lattice parameters. The deviation from cubic symmetry
reflects the noncubic ordering of gamma alumina in agree-
ment with the measured x-ray diffraction (XRD) powder
patterns in this compound. We suggest that our locally noncu-
bic model should give good predictions for real gamma
alumina since the properties of materials with a certain de-
gree of disorder are governed by local structure. The calcu-
lated bulk modulus for γ-Al₂O₃ is 209 GPa, in good agree-
ment with the LDA value of 219 GPa obtained in a previous
work. For comparison, the lattice parameter predicted us-
ging CASTEP is 7.797 Å. This last result reflects the impor-
tance of internally consistent calculations using GGA-

<table>
<thead>
<tr>
<th>Property</th>
<th>Calculated (GGA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>C2/m</td>
</tr>
<tr>
<td>a=b(Å)</td>
<td>5.663</td>
</tr>
<tr>
<td>c/a</td>
<td>2.421</td>
</tr>
<tr>
<td>α=β(°)</td>
<td>90.6</td>
</tr>
<tr>
<td>γ(°)</td>
<td>60.401</td>
</tr>
<tr>
<td>Volume (Å³)</td>
<td>382.326</td>
</tr>
<tr>
<td>B₀(GPa)</td>
<td>209</td>
</tr>
<tr>
<td>Sites</td>
<td>u</td>
</tr>
<tr>
<td>Al(1)₉₄</td>
<td>0.0039</td>
</tr>
<tr>
<td>Al(2)₉₄</td>
<td>0.3247</td>
</tr>
<tr>
<td>Al(3)₉₄</td>
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<tr>
<td>Al(4)₉₄</td>
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</tr>
<tr>
<td>Al(5)₉₄</td>
<td>0.6511</td>
</tr>
<tr>
<td>Al(6)₉₄</td>
<td>0.1650</td>
</tr>
<tr>
<td>Al(7)₉₄</td>
<td>0.6756</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.8452</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.8346</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.4887</td>
</tr>
<tr>
<td>O(4)</td>
<td>0.6320</td>
</tr>
<tr>
<td>O(5)</td>
<td>0.6791</td>
</tr>
<tr>
<td>O(6)</td>
<td>0.8344</td>
</tr>
<tr>
<td>O(7)</td>
<td>0.4943</td>
</tr>
<tr>
<td>O(8)</td>
<td>0.0026</td>
</tr>
<tr>
<td>O(9)</td>
<td>0.3351</td>
</tr>
<tr>
<td>V₁₀₉₄</td>
<td>0</td>
</tr>
<tr>
<td>V₂₀₉₄</td>
<td>0.5</td>
</tr>
</tbody>
</table>

In addition, we have calculated the partial density of
states (PDOS) for the proposed bulk structure [O₆O₆(3)] as
well as its total DOS and the band structure (Fig. 3 and Fig.
4). The first clear feature from Fig. 3 is that almost all the
valence charge is associated with oxygen atoms, suggesting a
highly polar character of the Al-O bonding, consistent with
previous works on κ-Al₂O₃ and α-Al₂O₃.42,43 In fact, the
lower and upper valence bands are dominated by O-s and
O-p, respectively, with a small contribution from Al-s, -p,
and -d in each.

In Fig. 4 the electronic band structure of O₆O₆(3) shows a
direct band gap of 3.97 eV at the Γ point in contrast to the

FIG. 1. Calculated relative energies per unit formula after full
relaxation for the 17 nonequivalent structures for bulk γ-Al₂O₃ with
respect to the α-Al₂O₃. The horizontal dashed lines labeled as
ΔH(γ-α) and ΔH(δ-α) represent the experimental transformation
enthalpies of gamma and delta aluminas with respect to alpha
alumina, respectively.
The experimental value of 8.5 eV (Ref. 44) — a deficiency typical of DFT methods. Nevertheless, the predicted value is in excellent agreement with that obtained using LDA. The flatness of the bands in the top of the upper valence band (UVB), especially along the A-T-Z points, denotes the tightly localized bonding of the corresponding electrons to the host atoms. Besides, we also observed that the topmost bands are noticeably separate from the rest of the UVB. This special feature is related with the fact that $\gamma$-Al$_2$O$_3$ has a layered-like structure. As illustrated in Fig. 5, the electronic distribution of the highest UVB band in the energy range of 0–0.01 eV below the band gap shows high electronic localization on the O atoms nearest to the vacancy sites.

The Mulliken population analysis results for the $\Omega h O h s$ model of $\gamma$-Al$_2$O$_3$ is presented in Table II. For comparative purposes, we have carried out the same analysis on $\alpha$-Al$_2$O$_3$ as well. As mentioned in the previous section, the spilling parameter$^{39,40}$ ranged between 0.008 and 0.007, indicating a reliable projection to the LCAO basis set. In the $\alpha$-Al$_2$O$_3$ crystal, the Al-O overlap populations $n_m$(Al-O) are 0.34 and 0.27 e (mean=0.31 e) with bond lengths of 1.868 and 1.993 Å, respectively, with a mean of 1.924 Å. The effective ionic valence charge $(q_{d\Omega})$ is 1.38 e. These values, especially the overlap population $n_m$, measure the crystal ionicity: a higher value of $n_m$ means a higher degree of covalency in the bond. The results suggest that $\alpha$-alumina shows predominantly ionic bonding with a small level of covalency. The results for $\gamma$-Al$_2$O$_3$ are more involved due to the small deviation from the perfect spinel structure. A close inspection shows that the Al$_{T\Omega}$-O bonding is more covalent.
TABLE II. Mulliken population analysis for α-Al₂O₃ and γ-Al₂O₃. The averaged effective ionic charge ($\bar{q}_{\text{eff}}(\alpha)$) and overlap population ($\bar{n}_{\text{m}}(\alpha-O)$) are in e units while the averaged bonding distances ($\bar{d}$) are in Å.

<table>
<thead>
<tr>
<th>System</th>
<th>$\bar{q}_{\text{eff}}(\alpha)$</th>
<th>$\bar{n}_{\text{m}}(\alpha-O)$</th>
<th>$\bar{d}(\text{Al-O})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Al₂O₃ : Al₀₃</td>
<td>1.38</td>
<td>0.31</td>
<td>1.92</td>
</tr>
<tr>
<td>γ-Al₂O₃ : Al₀₃</td>
<td>1.39</td>
<td>0.33</td>
<td>1.94</td>
</tr>
<tr>
<td>γ-Al₂O₃ : Al₁₃</td>
<td>1.28</td>
<td>0.49</td>
<td>1.81</td>
</tr>
</tbody>
</table>

than the Al₂O₃-O. Comparison with the overlap population values for α-Al₂O₃ suggests to us that gamma is less ionic than alpha alumina.

IV. ENERGETICS AND STRUCTURAL PROPERTIES OF γ-Al₂O₃ SURFACES

A. Surface energies

Having resolved a likely structure for bulk γ-Al₂O₃, we proceed to investigate the (1 1 1), (0 0 1), (1 1 0), and (1 5 0) surfaces. The cleaving planes were chosen in such a way to cross the maximum amount of Al-vacancy sites. That is the reason why the rather high index (1 5 0) surface appears as a viable choice. In particular along {1 1 1} we consider two surfaces: cleaving through the $V_{100}$-Al(3)$_d$ plane yields (1 1 1)$_a$, while the $V_{200}$-Al(4)$_d$ plane is denoted (1 1 1)$_b$ (Fig. 2). Note that [1 1 1], [0 0 1], and [1 5 0] in the cubic system are equivalent to [0 0 1], [1 1 0], and [1 1 1], respectively, in the cell displayed in Fig. 2. In order to minimize the dipole moment in the supercells, we built the slabs with similar surfaces in each side of the slab and kept Al₂O₃ stoichiometry throughout.

The k-point mesh depended on the slab under study: for (1 1 1), (0 0 1), (1 1 0), or (1 5 0) we used a k-point mesh including $\Gamma$ of $(2 \times 2 \times 1)$, $(2 \times 4 \times 1)$, $(2 \times 3 \times 1)$, and $(4 \times 2 \times 1)$, respectively, in order to converge the slab total energy to $<5$ meV/atom. Furthermore, our tests show that a vacuum of 10 Å is adequate to eliminate the surface-surface artifact interaction. Using the standard method, we subtract the surface energy per unit area ($\sigma$) of the slabs with the equation

$$\sigma = \frac{1}{A} \lim_{N \to \infty} \frac{1}{2}(E_{\text{surf}}^N - NE_{\text{bulk}}),$$

where $A$ is the slab area, $E_{\text{surf}}^N$ is the total energy of the $N$-atom slab, and $E_{\text{bulk}}$ is the bulk total energy. Here the limit is approximated with the $Nth$ term. However, rather than use $E_{\text{bulk}}$ from the calculations of Sec. III, we use the more consistent value given by the slope of the linear polynomial fitted to $E_{\text{surf}}^N$ versus $N$, as suggested in previous works.

When the convergence is reached there is a linear dependence of $E_{\text{surf}}^N$ with respect to $N$,

$$E_{\text{surf}}^N \approx 2A\sigma + NE_{\text{bulk}}.$$  

So, the slope is the bulk energy, which is then replaced in Eq. (1) to yield the surface energy. We calculated the energy of several slabs with different thicknesses, keeping Al₂O₃ stoichiometry throughout. In order to obtain an accurate interpolation in Eq. (2) for $E_{\text{bulk}}$ and then to obtain $\sigma$, we carried out full relaxations on the internal coordinates of slabs containing 40, 80, and 120 atoms for the (1 1 1) slabs; for the (0 0 1), (1 1 0), and (1 5 0) slabs we used 80 and 100 atoms. We observed metallic behavior in some of the relaxed slabs, but on complete optimization of the ions, the ground state becomes insulating. We would like to stress the fact that the computed surface energies are convergent values that have become independent of the number of atoms [$N$ in Eqs. (1) and (2)].

Considering convergence with respect to slab thickness, we found that for the (1 1 1)$_a$ and $b$ surfaces, 40-atom (eight layer) slabs were adequate to converge the surface energy to $<0.07$ J/m$^2$, while for the others, 80- or 100-atom slabs were needed in order to keep the same convergence. From our calculations, (1 1 1)$_a$ is the most stable surface with $\sigma_R = 0.95$ J/m$^2$ and its enhanced stability is discussed below; the next stable surface is (0 0 1) with $\sigma_R = 1.05$ J/m$^2$ (see Table III). Following the same method for estimating the surface energy using CASTEP, the (1 1 1)$_a$ energy is 1.04 J/m$^2$ in good accordance with the VASP predicted value.

It is useful to compare our γ-(1 1 1) surfaces with the well-characterized (0 0 0 1) basal plane of α-Al₂O₃, since this also shows close-packed O layers. Using our model for bulk α (Sec. III) and following published work, we generated a slab model for the Al-terminated (0 0 0 1) surface. Convergence of $\sigma$ to $<0.05$ J/m$^2$ was achieved with respect to slab thickness (six layers, 13.1 Å), vacuum thickness (13.1 Å) and k-point mesh (2 × 2 × 1) including $\Gamma$. Interpolation across ≈60-atom slabs yields $\sigma_R = 1.54$ J/m$^2$.

The total energy of a solid sample is the sum of bulk and surface contributions. Since γ-alumina shows a lower surface energy than α-alumina, but higher bulk energy, there must exist some critical molar surface area $A$ at which the two polymorphs show the same total energy and are in thermodynamic equilibrium. Using our calculated values of $\Delta\sigma(\alpha-\gamma) = +0.59$ J/m$^2$ and $\Delta E_{\text{bulk}}(\alpha-\gamma) = -0.178$ eV/Al₂O₃ = −17.2 kJ/mol yields a critical $A$ of about 29 000 m$^2$/mol or 290±10 m$^2$/g (the latter obtained using the molar mass of 102 g/mol). A lower value, $A = 125$ m$^2$/g, is reported from high-temperature calorimetry of hydrated aluminas, in agreement with molecular dynamics simulations.

Commercial samples of γ-Al₂O₃ show surface areas ranging from 75–250 m$^2$/g. Our calcula-

TABLE III. Calculated α-Al₂O₃ (0001) and γ-Al₂O₃ surface energies for relaxed ($\sigma_R$) and static ($\sigma_s$) slabs.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Slab size (atoms)</th>
<th>$\sigma_R$(J/m$^2$)</th>
<th>$\sigma_s$(J/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-(0 0 0 1)</td>
<td>60</td>
<td>1.54</td>
<td>3.15</td>
</tr>
<tr>
<td>γ-(1 1 1)$_a$</td>
<td>40</td>
<td>0.95</td>
<td>1.62</td>
</tr>
<tr>
<td>γ-(1 1 1)$_b$</td>
<td>40</td>
<td>1.85</td>
<td>3.57</td>
</tr>
<tr>
<td>γ-(0 0 1)</td>
<td>100</td>
<td>1.05</td>
<td>2.97</td>
</tr>
<tr>
<td>γ-(1 1 0)</td>
<td>100</td>
<td>1.53</td>
<td>3.43</td>
</tr>
<tr>
<td>γ-(1 5 0)</td>
<td>80</td>
<td>1.91</td>
<td>2.79</td>
</tr>
</tbody>
</table>
tions indicate that alumina of slightly higher porosity, with an internal surface area >300 m²/g, would be thermodynamically stable as the γ polymorph.

With growing interest in ultrathin films of alumina for electronics applications, we note that films <9 Å thick also show surface areas of >300 m²/g. This estimate assumes an averaged density of 3.8 g/cm³ and neglects interfacial interactions, which may in fact dominate in such a thin film. Transition phases, such as γ-Al₂O₃, will therefore be thermodynamically favored during the early stages of film deposition (9 Å represents about four alumina layers). Thicker γ-Al₂O₃ films will be metastable, producing α-Al₂O₃ when annealed.

B. Surface structure

Starting from the bulk perfect sites we carried out a full ionic relaxation of the atoms in the slab until the forces were less than 0.03 eV/Å. Figures 6–8, 10, and 11 show the outcome of such relaxations plotted as a function of depth within the slab. In these figures, the projection of the marks onto the depth axis represents the final position of the oxygen and aluminium sublattice planes normal to the surface with respect to the most superficial atom, revealing how the Al and O layers are arranged. On the other hand, the x axis represents the ionic displacements normal (δz) and parallel ([δx,y]) to the surface of the oxygen and aluminium atomic layers with respect to their perfect sites in the bulk.

In order to have a reference point, consolidate our method, and understand properly the ionic relaxations, we are going to analyze thoroughly the (0 0 0 1) α-alumina as presented in Fig. 6. Al and O layers are quite clear: MO₃/M/M/O₃/M/M/O₃. Trigonal symmetry constrains the surface O in [0 0 0 1] (δz displacements for O are negligible as shown in Fig. 6 left panel), so that the relaxation of the topmost Al into a near-trigonal site can only be accommodated by twisting within (0 0 0 1) (δx,y)=0.07–0.08 Å, as described in Ref. 8. The coverage of trigonal Al atop the close-packed O layer is 8.4 μmol/m².

From the left panel of Fig. 6 one can deduce the interlayer relaxations with respect to the corresponding bulk spacings. For instance, the topmost Al (depth=0 by definition) has a relaxation δz=−0.69 Å, where the minus sign means that the movement was towards the bulk. Therefore, the original position of this Al was 0.69 Å above the surface. The first O layer at 0.12 Å deep, had an outward relaxation δz=0.03 Å (i.e., the initial depth was 0.15 Å below the surface). From these data one can derive M-O₃ distances; the initial was
0.84 Å and the final is 0.12 Å, giving an M-O₃ change of −0.72 Å or −86%. If we apply the same analysis to all the layers in the slab, we finally find: −86, +4, −42, +21, and +6% for the first five layers M-O₃, O₃-M, M-M, M-O₃, and O₃-M, respectively. This result is in good agreement with previous theoretical and experimental results. We note that shifting the topmost Al to other, less symmetrical surface sites results in reconstruction and a >2 J/m² increase in σ.

C. Structure of the (1 1 1) surface

The (1 1 1)a surface (Fig. 7) has a $M^{111}$O₄ termination where the surface metal atoms are threefold coordinated [see Fig. 7(b)], with a layer ordering of $M^{111}$O₃/O₃$^{111}$/$M^{111}$d$^{111}$/$M^{111}$h$^{111}$/$M^{111}$d$^{111}$O₂/M₂$^{111}$. The most superficial Al atoms present a normal inward relaxation ($\delta$) with respect to their perfect sites of −0.3 Å with a small planar deformation ($|\delta_{xyz}|$) of 0.03 Å [Fig. 7(a)]. The four O atoms of the outermost close-packed layer (at ~0.05 Å deep) relax normal to the surface, rumpling by ~0.2 Å, so that there is little in-plane distortion ($|\delta_{xy}| < 0.05$ Å). The relaxed surface Al is near trigonal and shows a coverage of 5.95 μmol/m². In general, in the (1 1 1)a slab, the $\delta$ and $|\delta_{xyz}|$ relaxations of both Al and O atoms decrease to less than 0.07 Å when the atoms are more than 4 Å deep within the slab. From the left-hand panel of Fig. 7(a) the interlayer relaxation with respect to the bulk spacings were: −58, +4, +0.9, −74, and −5% for the $M^{111}$O₃, O₃-M$^{111}$, $M^{111}$O₃-O₂, O₂-M$^{111}$d, M$^{111}$d-M$^{111}$h, and M$^{111}$h-M$^{111}$d, respectively. It is important to mention that within the O₂ layer at 2.25 Å deep, the O atoms are threefold coordinated and show small deformations $|\delta_{xyz}| < 0.07$ Å. As Fig. 7(a) shows, the topmost Al is on an axis of threefold rotational symmetry with respect to the O and M$^{111}$h sublayers down to ~3.5 Å deep.

At first glance, the (1 1 1)b surface appears similar to (1 1 1)a: it has a $M^{111}$O₃ termination with a layer ordering of $M^{111}$O₃/O₄$^{111}$/$M^{111}$h$^{111}$/$M^{111}$d$^{111}$O₂/M₂$^{111}$, as shown in Fig. 8. The topmost Al has relaxed $\delta_{z} = −0.9$ Å from its octahedral position into an almost trigonal site, flush with surface O, with relatively little sideways deformation ($|\delta_{xyz}| = 0.3$ Å). However, the distortion in the subsurface layers is an order of magnitude larger in (1 1 1)b than in (1 1 1)a. The O’s at 0.0 and 0.5 Å deep are twofold coordinated ($|\delta_{xyz}| = 0.2$ −0.4 Å); the Al at 1 Å deep is five coordinate ($\delta_{z} = +0.3$, $|\delta_{xyz}| = 0.4$ Å), and only 2.6 Å from the topmost Al. The interlayer $M^{111}$h-O₃, O-M$^{111}$d, M$^{111}$d-M$^{111}$h, M$^{111}$h-O₄, and distances undergo variations of −86, −62, −41, +87, −41, and −1%, respectively. Consistent with these severe distortions, we note that the topmost Al in (1 1 1)b does not lie on an axis of symmetry with respect to subsurface Al.

The outcome of the MD simulation for the (1 1 1)a surface shows no important structural changes. Analysis reveals MSD in the (1 1 1)a slab of 0.025 and 0.023 Å² for the superficial Al and O layers, respectively, while for the bulk-like Al and O layers at more than 3.5 Å deep [Fig. 7(a)] the MSD are 0.012 and 0.016 Å², respectively.

1. Electronic structure of the (1 1 1) surface

Mulliken analysis was carried out for the most stable γ-Al₂O₃ surface, (1 1 1)a. The effective charge and overlap population values exhibit only minor changes compared with the bulk. A direct comparison of the effective charges of the atoms in the first layer with the corresponding atoms in the bulk (Table II) show no significant changes, except for the most superficial Al and the four O belonging to the first layer with $q_{eff}(surf)−q_{eff}(bulk)=−0.14$ e and 0.04 e, respectively, i.e., there is a slight electron transfer from the three-coordinated Al to the first layer of O. We find no appreciable
change in the Al-O overlap population within the first layer, meaning that, in spite of the considerable inward relaxation, there is no increase in the covalency of the surface.

We have carried out a GGA calculation of the band structure of the \( \gamma \)-slab, and this is shown in Fig. 9. Energies were aligned by matching the O semicore \( s \) states of the lower VBs of slab and bulk. A detailed comparison of the upper VBs showed that no surface states intrude into the bulk band gap (Fig. 4). For this reason, the surface projection of the bulk upper VB is omitted from Fig. 9. For the slab, the states at the top of the upper VB exhibit high electronic localization mainly on the oxygens at 0.2 Å deep. Indeed the electronic density distribution of the highest occupied slab states reveals only small changes with respect to the corresponding state in the bulk, i.e., the electrons remain tightly bound to O atoms, as shown in Fig. 5.

Recognizing that GGA is quantitatively unreliable for excited states, we limit ourselves to qualitative features of the conduction band (CB). The surface-projected bulk CB is drawn in dashed lines in Fig. 9. It is evident that the band gap decreases at the surface (3.39 eV) relative to the bulk, due to a low-lying CB surface state. Analysis reveals that this state is localized on the topmost trigonal Al, similar to the established data on \((0001)\alpha-Al_2O_3\) (Ref. 8). Overall, the reduced dispersion of the surface CB relative to the bulk indicates that excited electrons at the surface will have larger effective mass.

From a direct comparison between the lowest empty surface state of \((0001)\alpha\)-alumina and \((111)\gamma\)-alumina, 4.8 and 3.4 eV above the Fermi level respectively, we predict \textit{a priori} that surface Al on \(\alpha-(0001)\) is less reactive than that on \(\gamma-(111)\).

D. Structure of the \((001)\) surface

The \((001)\) surface undergoes large reconstruction on relaxation (Fig. 10). Returning to our model of bulk \(\gamma-Al_2O_3\), two types of stoichiometric \((001)\) layers separated by \(\sim 2\) Å can be identified: \(M_{6}^{O}M_{2}^{O}O_{12}\) and \(M_{4}^{O}M_{4}^{O}V_{2}^{O}O_{12}\). Cleaving through the vacancies of the latter yields a 100-atom bulk-terminated slab, which is our starting structure. A feature of this termination is highly undersaturated surface Al [two-coordinate, formerly \(T_{d}\), Al(1) and Al(2) in Fig. 10(a)]. These

FIG. 9. Calculated \((111)\alpha\) surface band structure of \(\gamma-Al_2O_3\). The bands in dashed lines are the surface-projected bulk conduction band structure. The zero of energy corresponds to the bulk UVB maximum (dotted-dashed line).

FIG. 10. (a) Outcome of ionic relaxations for the \((001)\) surface as a function of depth within the slab and a view of its structure. Notice the arrows that show the ionic relaxations and stress the site exchange: Al(4), Al(5) and Al(3), Al(6). (b) Top view of this surface. The numbers in (a) and (b) are in correspondence.
Al atoms are unstable and relax into five-coordinate surface sites. This in turn precipitates a spontaneous \( O_{\text{Av}} - T_{\text{Al}} \) exchange at the surface, with other Al in adjacent (1 1 0) planes relaxing in opposite directions into nonspinel sites [Al(4), Al(5) and Al(3), Al(6) in Fig. 10]. As the figure shows, Al displacements are as much as 1 Å. It is important to note that atoms of the subsurface and central slab layers undergo much smaller displacements, so that we are confident that they remain bulklike.

Edge-linked [0 0 1]-oriented Al\(_{\text{Av}}\)O\(_4\)-Al\(_{\text{Td}}\) is thus generated just below the surface, showing short Al-Al (2.6–2.7 Å, about 1 Å less than in the bulk). This means that in the adjacent (100) plane a subsurface octahedral vacancy is opened up while the surface \( V_{O_{\text{Av}}} \) has been eliminated. The three-atom-linked Al displacements [Al(1)-Al(4)-Al(5) and Al(2)-Al(3)-Al(6) in Fig. 10(b)] have thus effected a net \( V_{O_{\text{Av}}} \) migration of 3.8 Å diagonally away from the surface and towards bulk \( V_{O_{\text{Av}}} \) giving \( V_{O_{\text{Av}}} \) of just 2.5 Å.

With two such three-atom-linked displacements occurring per unit cell, we observe the generation of one tetrahedral vacancy in the space between. We therefore denote the layers as

\[
M_6^{10b}V_{\text{Td}}/O_{\text{12}}/M_2^{10b}/M_2^{10b}/V_2^{10b}O_{\text{12}}/M_2^{10b}/M_2^{10b}/M_2^{10b}/V_2^{10b}O_{\text{12}}/M_2^{10b}
\]

(where the topmost \( M_6^{10b} \) are in fact five coordinate). Reflecting the migration of \( V_{O_{\text{Av}}} \) away from the surface, a surface of predominantly five-coordinate Al\(_{\text{Av}}\) is favored, at a coverage of 10.44 \( \mu \)mol/m\(^2\). Fully coordinated Al\(_{\text{Td}}\) do occur as well [atoms Al(5), Al(6)] and result in rumpling in the Al sublattice of 0.8 Å.

We considered an alternative arrangement of superficial Al\(_{\text{Td}}\) as a starting structure [a in Fig. 10(b)]. A similar pattern of Al exchange was observed on relaxation, to give a surface energy of 1.24 J/m\(^2\) (structure not shown).

The outcome of the MD simulation for the (0 0 1) surface shows no important structural changes. The MSD for the Al and O layers on the surface are 0.018 and 0.020 Å\(^2\), respectively, and for the bulklike Al and O layers at more that 3.3 Å depth [Fig. 10(a)] these values are 0.017 and 0.018 Å\(^2\), respectively.

E. Other surfaces

We have computed two different (1 1 0)-terminated slabs, both 5.6 Å thick (80 atoms for an Al\(_{\text{Av}}\)-terminated slab and 100 atoms for a mixture of both Al\(_{\text{Av}}\) and Al\(_{\text{Td}}\) before relaxation) and observe that both surfaces undergo massive reconstruction into open, amorphous structures. Interestingly, the 80-atom slab, with \( \sigma=1.53 \) J/m\(^2\), displays a sawtooth surface structure (Fig. 11), which we interpret as microfacets along (1 1 1) and (1 1 1). Al shows fivefold coordination within the (1 1 1) facets and three/four coordination within (1 1 1). The creation of these small planes after optimization supports the (1 1 1)a surface as the most stable bare surface. The 100-atom slab with lower surface energy shows no sawtooth surface and a lower surface energy (\( \sigma=1.46 \) J/m\(^2\) in Table III), consistent with the smaller \( \delta_z \) displacements than in the 80-atom slab. This result points out the relation be-

tween the presence of Al\(_{\text{Av}}\) atoms on the surface and its stability. Although not shown in Fig. 11, we found that (1 1 0) has high porosity, perhaps related with the position and orientation of the \( V_{O_{\text{Av}}} \) vacancy sites.

Examination of the (1 5 0) superficial atoms after relaxation reveals Al with two-, three-, and fivefold coordination (not illustrated here). The outermost O undergo large deformations \( [\delta_{\text{xyz}}] \) of 0.88 Å with small \( \delta_z \) of +0.28 Å; the same behavior is found for the twofold coordinated O at 1.12 Å deep with relaxations \( [\delta_{\text{xyz}}] (\delta_z) \) of 0.83 (+0.032) Å. We observe the largest deformation \( [\delta_{\text{xyz}}] =1.2 \) Å of the Al\(_{\text{Td}}\) at 0.7 Å deep, while the remaining Al atoms down to 1.6 Å deep have relaxations of \( <0.38 \) Å.

V. DISCUSSION

We present an extensive study of stoichiometric \( \gamma \)-alumina surfaces. Three of these are composed of close-packed O: \( \gamma-\{1 1 1\}a \), \( \alpha-(0 0 0 1) \), and \( \gamma-(1 1 1)b \) (Figs. 6–8), with surface energies of 0.95, 1.54, and 1.85 J/m\(^2\), respectively. The range of stabilities can be rationalized by looking at the Al sublattice and its effect on the O layers. The topmost Al lies in all cases over a subsurface cation vacancy and so relaxes into an almost trigonal site within the O layer, lowering the surface dipole moment. In this respect, our results agree with many other calculations, where Al-Al interactions are found to govern the relaxation of undercoordinated Al.\(^{8,28,30}\) No other Al atoms show substantial displacements. If the coverage of trigonal Al is low and if the trigonal Al is symmetrical with respect to subsurface Al, then this relaxation can be accommodated with minimum distortion of the O layer, giving a stable surface, such as \( \gamma-\{1 1 1\}a \). The interaction between trigonal Al and a disordered arrangement of cations beneath the surface is destabilizing, as is the case in \( \gamma-(1 1 1)b \).

The computed electronic structure shows that bonding at the (1 1 1) surface is similar to that in bulk \( \gamma-Al_2O_3 \) (Sec. III), where we find that Al\(_{\text{Td}}\) is bound slightly more covalently than Al\(_{\text{Av}}\). A low-lying CB state is localized on the trigonal Al of (1 1 1), a consequence of its coordinative undersaturation and mobility in \( z \), which means that the trigonal Al behaves as a strong Lewis acid and as the adsorption site for electron-rich molecules.

Simply to preserve stoichiometry, the surface Al coverage decreases from \( \alpha-(0 0 0 1) \) to \( \gamma-(1 1 1) \), consistent with the lower density of reactive sites on the latter,\(^{48}\) and the surface is stabilized as the coverage decreases. Extrapolating this trend to more disordered transition aluminas, we expect that...
they will show an even lower density of surface Al above close-packed O, and a correspondingly lower surface energy. However, this must be offset by the energetic penalty of deformations in subsurface Al and O, which we predict should accompany a disordered Al sublattice [as calculated for γ-(1 1 1)h]. A low density of trigonal Al within (1 1 1) surfaces may explain the lack of three-coordinate Al measured by NMR.

The (0 0 1) surface is computed to behave differently to (1 1 1). The loose, square arrangement of O anions permits considerable flexibility in the surface Al, most of which relax into neighboring nonspinel sites (Sec. IV D) and octahedral vacancies are repelled from the (0 0 1) surface into the slab interior, as in Ref. 27. However, by calculating a larger slab than Ref. 27 (in x as well as z), we find that surface reconstruction can occur without destruction of the slab, and we are able to identify the barrierless three-atom-linked exchange mechanism that displaces O$_{slab}$ towards the bulk. This facile motion and undercoordination means that both five-coordinated and tetrahedral Al are moderate Lewis acids.

However, we are aware that the pattern of Al$_{O_h}$, Al$_{T_d}$, and V$_{T_d}$ which we obtain is not correlated with the subsurface structure, and is probably an arbitrary product of our choice of cell. Other arrangements atop the cubic substrate would probably be isoenergetic, as long as the 6:2 ratio of five-coordinate Al to Al$_{O_h}$ is preserved. Our finding of Al$_{T_d}$ close to the surface is supported by solid-state NMR of γ-Al$_2$O$_3$ (Ref. 24) and by FT-IR, although NMR indicates a slightly higher proportion of (6:3:1) amplitudes for the atoms at the surface in the (1 1 1)α and (0 0 1) surfaces, one can estimate the root-mean-square displacements (RMSD) that, for a simple harmonic oscillator, are related to its vibrational amplitude. We thus obtain amplitudes for the atoms at the surface in the (1 1 1)α and (0 0 1) slabs of 1.3 and 1.05 times larger than those in the bulk, respectively. Considering the close similarity in structure of (1 1 1)α γ-alumina and (0 0 0 1) α-alumina, our approximate value of 1.3 is in accordance with the value of 1.55 founded previously for (0 0 0 1) α-alumina.

We find that the (1 1 0) and (1 5 0) polar terminations are unstable. The relaxed (1 1 0) surface is rough, with O$_{h}$ vacancy sites remaining at the surface, and when there are no Al$_{O_h}$ atoms on the unrelaxed slab, the surface reconstructs by microfaceting into (1 1 1)-related segments. This is at odds with the results of Ref. 28, which are based on a hydrogen spinel in a thinner slab with frozen atoms. Our study is far from exhaustive however, and we recognize that other more stable (1 1 0) surfaces may exist.

The (0 0 1) and (1 1 1)α surfaces are found to be equally stable, with surface energies that differ by just 0.1 J/m$^2$, which is close to the limit of computational accuracy. These are purely thermodynamic considerations: the kinetics of various methods of alumina preparation (e.g., dehydration of boehmite, oxidation of metal) may favor other surfaces. Because of their metastability and microporosity, it is hard to prepare well-defined γ-Al$_2$O$_3$ surfaces under controlled conditions. A few such measurements are reported and indicate that (0 0 1) and (1 1 0) occur on γ-Al$_2$O$_3$.

Density-functional theory has been applied to the quantitative elucidation of structure and energetics of low index surfaces of transition aluminas. Surface energies of 1.00±0.05 J/m$^2$ were computed for both (1 1 1) and (0 0 1) surfaces of the γ-Al$_2$O$_3$ crystal, and so we conclude that either surface could occur. It follows that γ-Al$_2$O$_3$ films are thermodynamically stable with respect to α-Al$_2$O$_3$ up to a thickness of about 9 Å. Some less stable surfaces reconstruct so as to produce (1 1 1) microfacets. (1 1 1) surfaces are computed to be mostly O terminated, with a low coverage of trigonal Al behaving as a strong Lewis acid. The (0 0 1) surface is highly reconstructed to give Al in nonspinel sites; it is dominated by five-coordinate Al, with some tetrahedral Al, both of which are expected to be weaker Lewis acids. Given the high-level theoretical treatment and good agreement with experiment, these models may reliably represent a range of transition alumina surfaces.

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AB INITIO STUDY OF $\gamma$-Al$_2$O$_3$ SURFACES