

Atomic and electronic structure of the corundum (α -alumina) (0001) surface

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Using a tight-binding, total-energy model, we predict the atomic and electronic structure of the relaxed (1×1) corundum (0001) surface. The surface shows a large, bond-length-conserving relaxation, which is allowed by the topology of the surface. The relaxation is driven by a rehybridization of the surface Al atoms to sp^2 , and an accompanying drop in the energy of occupied surface states, during the relaxation. Displacements of surface atoms from bulk positions are as large as 0.7 Å, and should be observable using a low-energy electron diffraction intensity analysis. Full relaxed atomic positions are reported, as well as a wavelength-resolved surface band structure, including orbital characters of surface states.

I. INTRODUCTION

Corundum (the α phase of alumina, Al_2O_3) is one of the most widely used substrates for the growth of thin metal, semiconductor, and insulator films for both basic research and microelectronics applications.¹ Because of the importance of this material, its bulk, surface, and interfacial properties have been widely studied.

Low-energy electron-diffraction (LEED) studies of the (0001) basal plane surface showed that at low temperature (less than 1250°C), this surface has a (1×1) relaxed atomic structure in both air and vacuum.²⁻⁶ (Annealing at higher temperatures leads to more complicated structures.) The electronic structure of the (0001) surface has also been examined using ultraviolet photoemission spectroscopy (UPS) and x-ray photoemission spectroscopy (XPS).⁷ These studies show that the upper valence-band region is composed mainly of oxygen 2p states, and show no occupied states in the fundamental band gap. As yet, however, there are no published experimental measurements of the relaxed (0001) surface atomic positions.

This surface has been studied theoretically using local-density,^{1,8} Hartree-Fock,⁹ and empirical classical potential^{10,11} methods. However, to our knowledge no previous quantum-mechanical study of the (0001) (1×1) relaxed surface has reported predictions of the following properties: the full, relaxed surface-atomic positions, including displacement from bulk positions transverse to the surface; a quantum-mechanical explanation of the surface relaxations in terms of orbital rehybridization; and wavelength-resolved surface electronic band structure (including the orbital character of surface states) which could be compared to angle-resolved spectroscopic data.

In this paper we investigate these issues using a tight-binding, total-energy method. We find that the corundum (0001) (1×1) relaxation involves a large, bond-length-conserving displacement of the surface atoms from their bulk positions. This allows surface-layer aluminum atoms to rehybridize into a nearly perfect sp^2 bonding arrangement with neighboring oxygen atoms. We show that this relaxation is driven by lowering the en-

ergies of occupied surface states as those states rehybridize. This type of large relaxation is well known in simple compound semiconductor surfaces,¹² but to our knowledge this is the first such example among insulators with complicated bulk structures.

We begin by briefly reviewing the bulk properties of corundum. We next describe a tight-binding, total-energy model which is parametrized to reproduce known electronic and mechanical properties of the bulk. This model is then applied to the (0001) surface, providing predictions of the (1×1) relaxed surface atomic and electronic structure. Finally, the results are interpreted in terms of local surface topology and bonding environments.

II. CORUNDUM BULK PROPERTIES

Corundum has a complicated bulk structure, difficult to visualize from two-dimensional figures and brief descriptions. Because of this, and because of the large number of accessible papers which describe that structure in detail, we will only review relevant material briefly. Readers interested in a more detailed and lengthy description of the structure may consult Refs. 1, 9, and 13.

Corundum has rhombohedral symmetry, with 15 atoms (three Al_2O_3 formula units) per primitive unit cell. Like all rhombohedral systems, by using a larger unit cell corundum can be treated as hexagonally symmetric. It is in terms of the hexagonal cell that atomic positions are usually given.¹³ Moreover, the two-dimensional hexagonal primitive unit cell of the truncated bulk (0001) surface is a cross section of the hexagonal bulk unit cell (hence the designation by hexagonal indices). For simplicity, then, we present all results here in terms of the hexagonal bulk cell.

Figure 1 shows the atomic positions within the hexagonal bulk cell. Each atom lies in one of 18 planes normal to the long axis of the cell. Twelve of the planes contain a single aluminum atom per unit cell per plane, and six contain three oxygen atoms (arranged in an equilateral triangle) per unit cell. Each aluminum atom is bonded to

six nearest-neighbor oxygen atoms in a distorted octahedron, while each oxygen atom is bonded to four aluminum atoms in a distorted sp^3 arrangement. There are two nearest-neighbor bond lengths; half of the Al-O bonds are 1.86 Å long, and half are 1.96 Å long.

The bulk electronic properties of corundum can be simulated with a tight-binding¹⁴ model which includes electronic Hamiltonian matrix elements between valence s and p orbitals on nearest-neighbor atoms. We obtained Hamiltonian matrix elements for corundum by modifying Harrison's universal parameters for Al and O (Ref. 15) to fit previously calculated band structures and densities of states^{16,17} of α -Al₂O₃. Values for these fitted parameters are given in Table I. The notation for the electronic parameters follows Slater and Koster,¹⁴ and has been described in detail by Harrison.¹⁵

Figure 2 shows the bulk band structure, and Fig. 3 the bulk density of states, calculated using the parameters in Table I. These adequately reproduce the previously calculated bulk properties.^{16,17}

The total energy per unit cell of bulk corundum can be modeled by the equation

$$E_{\text{tot}} = E_{\text{bs}} + U, \quad (1)$$

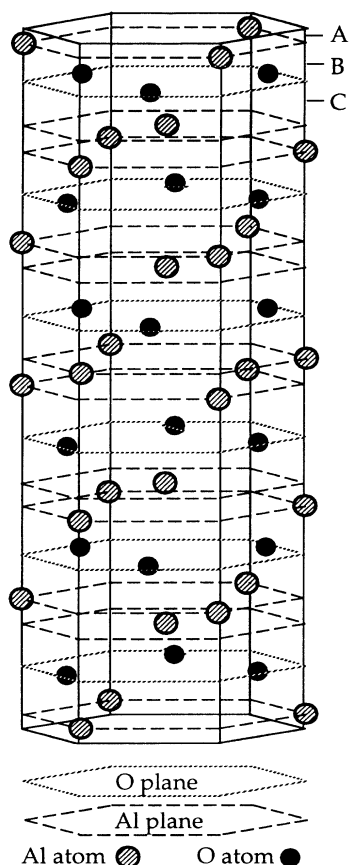


FIG. 1. Bulk structure of corundum. Solid lines show the boundaries of the hexagonal unit cell. There are only three distinct truncated bulk surfaces; these are formed by slicing the bulk with planes passing through points labeled *A*, *B*, and *C*, respectively.

TABLE I. Electronic Hamiltonian matrix elements, and interatomic repulsive potential parameters, used in the tight-binding, total-energy model for corundum. The notation for electronic parameters follows Slater and Koster (Ref. 14). Units are eV. O-Al electronic parameters are taken to have the same values as the corresponding Al-O electronic parameters. Symbols for repulsive parameters are explained in the text; units for c are eV, while n is dimensionless.

	O	Al	Al-O
ϵ_s	-29.14	-10.11	
ϵ_p	-14.13	-4.86	
$V_{ss\sigma}$			-3.117
$V_{sp\sigma}$			4.097
$V_{pp\sigma}$			7.214
$V_{pp\pi}$			-1.803
c			0.440
n			-10.285

where E_{bs} , the "band-structure" energy, is the sum of occupied eigenvalues of the tight-binding Hamiltonian integrated over the Brillouin zone, and U is a sum of two-body, nearest-neighbor repulsive potentials of the form

$$U_{ij} = c(r_{ij}/r_{0ij})^n, \quad (2)$$

where c and n are constant parameters, r_{ij} is the distance between nearest-neighbor atoms i and j , and r_{0ij} is the value r_{ij} takes in the bulk. The values used for c and n (given in Table I) are found by requiring the model to reproduce the correct bulk lattice constant and bulk modulus of corundum.

Once parametrized to the bulk properties, the tight-binding, total-energy model may be applied to a surface to find the relaxed surface-atomic and electronic structures. Similar models have provided impressive results for a wide variety of materials.¹²

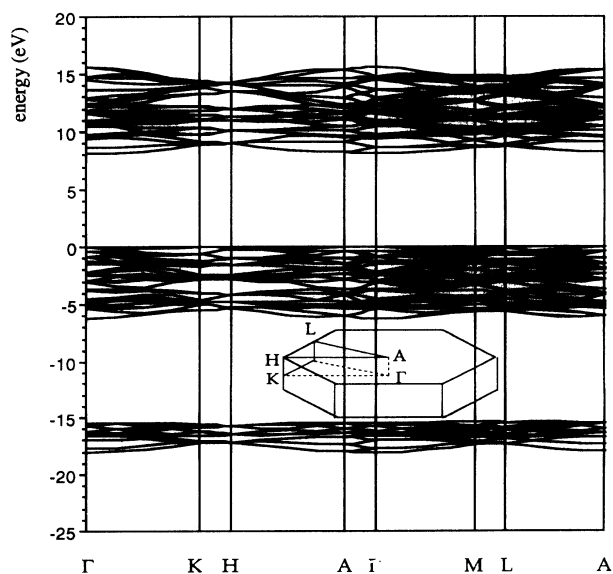


FIG. 2. Bulk band structure of corundum calculated from the tight-binding parametrization described in the text. The Brillouin zone is inset, with high-symmetry points labeled.

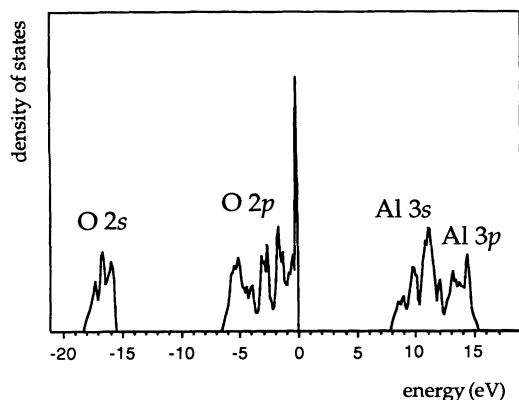


FIG. 3. Bulk density of states of corundum, calculated using the tight-binding model described in the text. Labels give orbital characters of states in various energy regions.

III. STABILITY AND ATOMIC STRUCTURE OF THE IDEAL CORUNDUM (0001) SURFACES

Before proceeding to the tight-binding, total-energy calculations for the corundum surface, we will first describe the atomic structure of the unrelaxed surface. An ideal (truncated bulk) basal plane surface can be formed by terminating the bulk along a plane normal to the long axis of the hexagonal bulk unit cell (Fig. 1). Crystallographically, there are only three possible terminations which lead to distinct surfaces. These are formed, respectively, by slicing the bulk with planes passing through points labeled *A*, *B*, and *C* in Fig. 1.

Only cleavage at *A* produces two equivalent surfaces. Moreover, local-density calculations¹ have shown that the aluminum-terminated surface *A* is the most stable. That this should be so can also be seen by applying the electron-bond-counting rules of Harrison¹⁸ to each of the three surfaces, to show that only surface *A* is "autocompensated," that is, both chemically stable and charge neutral. This argument, outlined in the following two paragraphs, is similar to the model of surface building blocks formulated by Guo, Ellis, and Lam¹ to explain the stability of this termination.

In the bulk, an Al atom has three valence electrons distributed among six bonds, so the Al atom can be thought of as contributing $\frac{1}{2}$ electron to each bond. Conversely, each O atom has six valence electrons and four bonds, giving $\frac{3}{2}$ electrons per bond, for a total of two electrons per bond from both Al and O neighbors. Now to create surface *A*, the lone surface Al atom per unit cell must have three bonds broken, leaving a total of $\frac{3}{2}$ electrons in cation dangling bonds. The three O atoms just below the surface Al plane each have one bond broken, leaving $\frac{3}{2}$ electrons in each of three anion dangling bonds. Each anion requires $\frac{1}{2}$ electron to create a nonbonding lone pair, for a total of $\frac{3}{2}$ electrons per unit cell; this is exactly what is provided by emptying the cation dangling bonds. Atoms on surface *A* can thus form a stable bonding environment, while remaining charge neutral, and this surface is therefore said to be autocompensated.

On the other hand, creating surface *B* requires breaking two bonds for each surface O atom, while no Al atoms have broken bonds. Three electrons are therefore required to create lone pairs on the oxygen atoms and form a chemically stable surface. There is, however, no available cation dangling bond charge density to do this. Surface *A* therefore cannot be both charge neutral and chemically stable (that is, it is not autocompensated), and hence should be unstable. A similar argument shows surface *C* to be unstable as well. For this reason, this study shall only consider the Al-terminated surface *A*.

The atomic surface of the ideal (0001) surface is shown schematically in Fig. 4. Like the bulk corundum structure, the ideal (0001) surface is difficult to describe briefly, and difficult to visualize from two-dimensional figures alone. However, the hexagonal symmetry of the surface unit cell (shown by dashed lines) is apparent. The surface is topped by a layer of Al atoms lying in a plane, with one Al atom per surface unit cell. Each Al atom is backbonded to three O atoms, all lying in a plane 0.8 Å below the surface Al atoms. Each of these O atoms are, in turn, backbonded to two Al atoms lying in different planes.

To help display the ideal atomic geometry deeper into the surface, Fig. 1 has been arranged so that the layer of Al atoms at the top of the cell correspond to the top Al layer on the ideal surface. Viewing the surface in this way points out an interesting complexity of the corun-

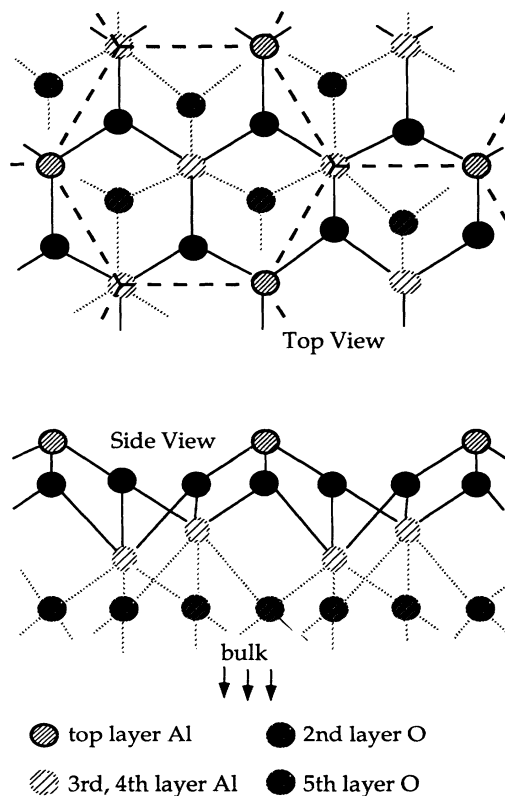


FIG. 4. Schematic illustration of the corundum (0001)-truncated bulk surface atomic positions. The boundaries of the surface unit cell are shown by dashed lines in the top view. Sub-surface atoms and bonds are shaded.

dum (0001) surface, compared to surfaces of materials with simpler structures. Suppose we construct a composite corundum (0001) atomic layer, infinite in two dimensions, by using unit cells like the one in Fig. 1 as building blocks. That is, a (0001) composite atomic layer is a two-dimensional hexagonal lattice whose unit cell is that shown in Fig. 1. The bulk can then be constructed by stacking equivalent composite (0001) layers, and a surface is left when we stop stacking. The point is that these composite layers are very thick, consisting of 18 distinct atomic planes. In contrast, when working with materials with simple bulk structures we are accustomed to thinking of crystallographically equivalent layers containing only one, or a few, atomic planes. To correctly visualize the ideal corundum (0001) structure, then, it is important to realize that no two planes of atoms shown in Fig. 4 are equivalent in the bulk, under any translation of bulk hexagonal unit vectors.

IV. RELAXED (0001) SURFACE-ATOMIC AND ELECTRONIC STRUCTURES

We model a corundum (0001) surface by a slab, periodic and infinite in the two dimensions parallel to the (0001) plane, consisting of a single composite (0001) atomic layer. As stated previously, one composite layer forms a thick slab, consisting of 18 atomic planes. Each side of the slab has an aluminum-terminated surface (described in Sec. III), so that the entire slab is charge neutral; the opposite sides of the slab are approximately 13 Å apart.

The total energy of the slab may be found by applying the tight-binding, total-energy model described in Sec. II. The relaxed surface-atomic positions are found by minimizing the total-energy functional Eq. (1) for the slab as a function of the atomic positions.

In this calculation, the (0001) surface atoms relax to a (1×1) structure shown schematically in Fig. 5. This relaxation involves a large, nearly bond-length-conserving displacement of atoms in the top two planes from their truncated bulk positions. The top-layer Al atoms move down toward the bulk, becoming nearly coplanar with their nearest O-atom neighbors, while the O atoms pucker outwards to keep the Al-O bond length approximately constant. In the relaxed surface, no nearest-neighbor bond length differs from its corresponding bulk value by more than 10%. The three O atoms remain coplanar.

Atoms below the first two (Al and O) atomic planes do not significantly relax from their bulk positions. This is an important indication that increasing the slab thickness would not significantly alter the calculated relaxed atomic positions; hence, the calculated positions well approximate the surface relaxation of a semi-infinite solid.

Figure 4 also defines a set of independent geometric parameters which quantitatively specify the relaxed atomic positions. Values for the parameters are given in Table II, and compared to those of the ideal surface, and to results of a previous local-density calculation.⁸ Note that the relaxed atomic positions differ from bulk atomic positions by as much as 0.7 Å for the surface Al atom. This is much larger than the typical resolution (about 0.1 Å) of LEED analysis for atomic displacements normal to the surface plane. The transverse displacements of the oxy-

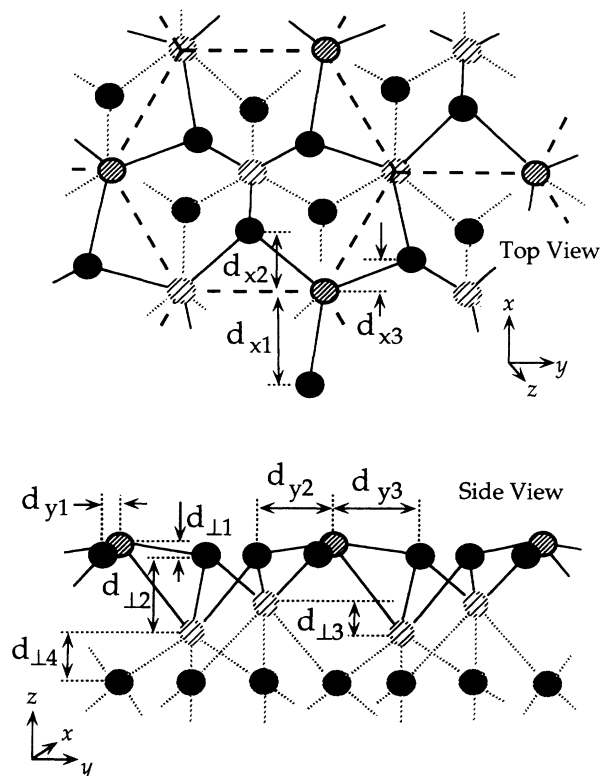


FIG. 5. Schematic illustration of the corundum (0001)-relaxed surface-atomic positions, calculated using the tight-binding, total-energy model described in the text. The surface shows a large, bond-length conserving displacement of the surface atoms from bulk positions, which allows the surface Al atoms to rehybridize to a nearly perfect sp^2 configuration.

gen atoms, however, are much smaller (approximately 0.2 Å). This length is comparable to the usual resolution of LEED analysis transverse to the surface.¹⁹ These displacements, however, may be measurable by ion-scattering techniques.²⁰

The relaxation can be understood from the (0001) surface topology and a simple picture of the Al atom bonding environment. Each top-layer Al atom is backbonded to three O atoms, and has lost three O neighbors when the surface was formed. By becoming coplanar with the O atoms, the Al atom has rehybridized into a sp^2 arrangement, which is more stable than the partial octahedron of the truncated bulk.

The rehybridization can take place because the topolo-

TABLE II. Values of geometric parameters (Fig. 5) for relaxed and unrelaxed corundum (0001) surfaces. Units are angstroms. The values are compared to LDA calculations (Ref. 8); hyphens denote values that were not reported in Ref. 8.

	d_{x1}	d_{x2}	d_{x3}	d_{y1}	d_{y2}	d_{y3}	d_{11}	d_{12}	d_{13}	d_{14}
unrelaxed	0.9	1.6	0.7	1.4	0.1	1.7	0.8	0.8	0.5	0.8
relaxed	1.1	1.8	0.7	1.5	0.2	1.5	0.1	0.8	0.6	0.8
LDA relaxed (approx.)	-	-	-	-	-	-	0.1	0.8	0.3	1.0

gy of the (0001) surface allows the Al atom to become coplanar with the O atoms while approximately conserving near-neighbor bond lengths. In directionally bonded systems such as semiconductors, large relaxations generally occur only when a bond-length-conserving motion of the surface atoms is allowed. This is because bond compression or elongation creates large local strain fields, incurring a large energy cost. While there are many examples of large, nearly bond-length-conserving relaxations among compound semiconductors,¹² to our knowledge this is the first such example among strongly insulating mineral oxide surfaces.

Figure 6 shows the calculated surface band structure. The reduced surface Brillouin zone is shown inset, with high-symmetry points labeled. Projected bulk bands are shown as shaded areas. Surface states were identified by finding solutions of the tight-binding Hamiltonian whose eigenvectors were localized near a face of the slab. This method gives qualitatively correct dispersion relations; differences in energy smaller than approximately 1 eV in Fig. 6 are not significant. Solid lines represent surface states of the unrelaxed surface, while dashed lines represent states of the fully relaxed surface.

The energies of electronic surface states for relaxed and unrelaxed surfaces show how the relaxation rehybridization lowers the surface energy. State S_2 is composed almost entirely of O $2p$ orbitals oriented transversely to the surface, while S_4 is mainly composed of O $2p$ orbitals oriented normal to the surface. These states are not significantly altered by the relaxation. On the other hand, the S_3 state (a mixture of transverse and normal O $2p$ components) and S_5 state (a mixture of Al $3p$ and $3s$ orbitals), mix upon relaxation (because the Al atom is rehybridizing to sp^2). This pushes the unoccupied S_5 state up out of the fundamental band gap, while lowering the energy of the occupied S_3 state by several electron volts. The occupied state S_1 , composed mainly of O $2s$ orbitals, also lowers its energy by mixing with orbitals on subsurface Al atoms.

It is worthwhile to point out that this model gives relaxed surface-atom positions similar to those predicted by classical potential models,^{10,11,21} but for a very different reason. In a two-body classical potential model, the surface Al and O atoms try to become coplanar to reduce a classical electric dipole moment of the top atomic layers, in the same way that the energy stored in a parallel plate capacitor can be lowered by moving the plates closer together. That this picture is not necessarily adequate is evidenced by the failure of classical potential models to predict the well-known surface-layer tilt of zinc-blende-structure semiconductor (110) surfaces, which is driven by quantum-mechanical energy lowering from rehybridization of surface atoms from their bulk configurations.¹² The tight-binding analysis of corundum shows a relaxation driven by similar quantum effect; that is, energy lowering from rehybridization of the surface-layer Al bonding environment from octahedral to sp^2 .

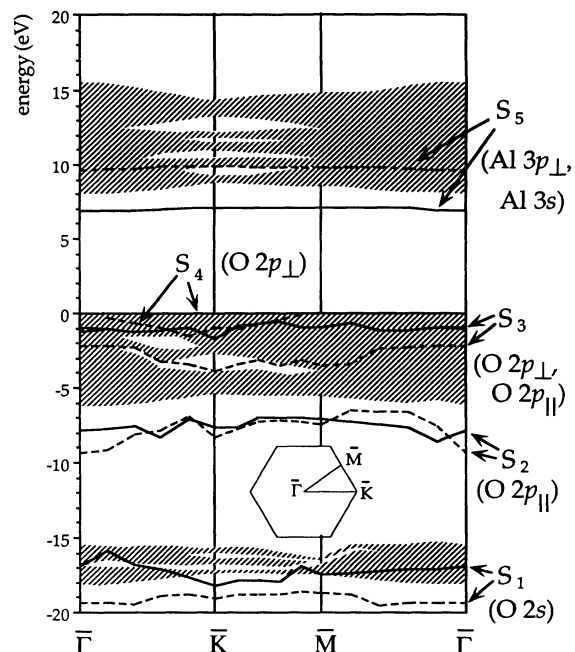


FIG. 6. Surface electronic states of the truncated bulk (solid lines) and relaxed (dashed lines) corundum (0001) surfaces, calculated using the tight-binding model described in the text. The reduced surface Brillouin zone is inset, with high-symmetry points labeled. Projected bulk bands are shown as shaded regions. Orbital characters of the various surface states are included with the respective surface state labels; the subscript " \perp " denotes a p orbital oriented normal to the surface plane, while " \parallel " refers to a p orbital oriented within the plane. These orbital characters refer to the unrelaxed surface; states mix during the relaxation (as described in the text).

V. CONCLUSIONS

The corundum (0001) surface has a large, nearly bond-length-conserving relaxation which lowers the surface energy by lowering the energies of occupied surface states.

This relaxation is analogous to the large relaxations of atomic positions at semiconductor cleavage surfaces, which can occur only when the surface topology allows bond-length-conserving motions of the surface atoms. Corundum is the first such example among mineral oxide insulators. This suggests that the chemical and topological principles which have been used so successfully to understand the structures of semiconductor surfaces are applicable to insulator surfaces as well.

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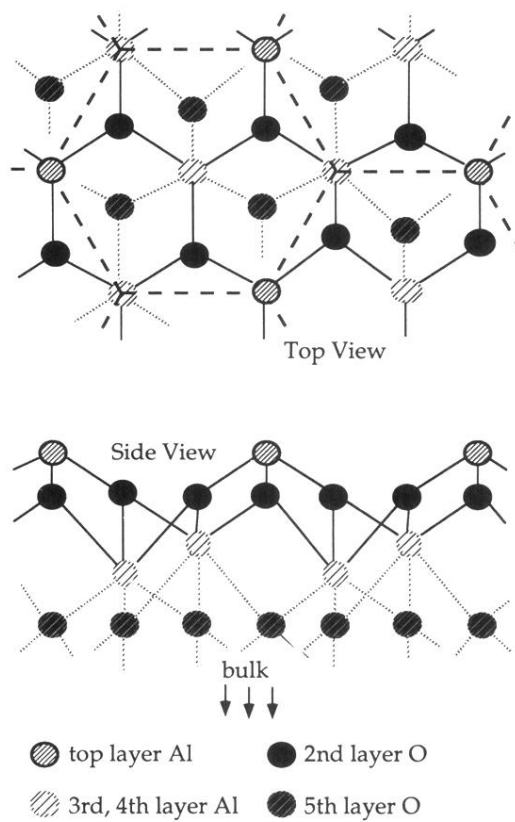


FIG. 4. Schematic illustration of the corundum (0001)-truncated bulk surface atomic positions. The boundaries of the surface unit cell are shown by dashed lines in the top view. Sub-surface atoms and bonds are shaded.