Stability of a Flexible Polar Ionic Crystal Surface: Metastable Alumina and One-Dimensional Surface Metallicity

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(Received 15 June 2001; published 16 May 2002)

A first-principles study of κ-Al_2O_3 (001) and $(00\bar{1})$ reveals new features of ion-surface stability and electronic structure. The need to generalize Tasker's rules for surface stability of low-symmetry crystals is shown. Structurally, the presence of bulk tetrahedral Al (Al^T) causes giant surface relaxations, with O termination at (001). Surface-layer Al^T are strongly unfavored. This is understood with Pauling's rules and thus generally applicable to metastable aluminas. The bulk charge asymmetry and Al-sublattice anisotropy caused by the Al^T create a 1D metallic surface state at $(00\bar{1})$.

DOI: 10.1103/PhysRevLett.88.226101 PACS numbers: 68.35.Md, 73.20.At

Ionic bonding is an old subject. In 1928 Pauling summarized the structural effects of electrostatics and quantum repulsion in a set of stability rules [1]. While simple ionic compounds, such as alkali halides, have few choices of stable arrangements, more complex ones, such as alumina (Al_2O_3), show a fascinating structural flexibility [2,3]. With its multitude of phases, Al_2O_3 has many applications: e.g., the stable α-Al_2O_3 in electronics and the metastable phases (γ, η, δ, θ, κ, ...) in applications characterized by surface properties (catalysis, coatings, adsorbents). However, metastability and poor crystallinity make experiments on metastable aluminas difficult [2] and theory needs quantum-mechanical (QM) methods to treat the subtle energy differences between the many structural possibilities [3,4]. So far, QM Al_2O_3 surface studies have focused on α-Al_2O_3 [5–8] and are scarce on metastable aluminas [9], due to uncertain structural information and/or disordered cation-sublattice structure [2,10,11]. Generally, the question of stability and atomic termination of ionic crystal surfaces has so far been addressed with the concept of "polar" surfaces [12], as originally formulated by Tasker [13]. He showed that a polar surface is electrostatically unstable but based his definition on an ideal, fully ionic, point-charge model, which is not obviously applicable to systems of partly covalent character and/or low symmetry.

This Letter reports on a structure and bonding determination of the (001) and $(00\bar{1})$ surfaces of κ-Al_2O_3, performed with first-principles density-functional theory (DFT). Because of the presence in most metastable aluminas of both tetrahedrally (Al^T) and octahedrally coordinated cations (Al^O) [2], these crystals present in general a lower symmetry than, for instance, α-Al_2O_3, which has only Al^O [1]. Our study, in addition to being the first characterization of the κ-Al_2O_3 surface, shows how Tasker's definition of surface polarity is insufficient in dealing with low-symmetry ionic crystals. Further, the κ phase is an ideal prototype for studies on the stability of metastable-alumina surfaces, thanks to its well-established atomic structure [3] and moderate amount of Al^T (1/4), which allows comparisons with α-Al_2O_3 to study the effects of the Al^T. The $\kappa(001)$ and $(00\bar{1})$ faces, obtained by cutting the crystal perpendicular to its main axis, are chosen as their structures are similar to the much-studied $\alpha(0001)$. The importance of κ-Al_2O_3 as a chemical-vapor deposited (CVD) coating on cutting tools, with preferential growth direction along [001] and/or $[00\bar{1}]$ [3], gives further motivation. Finally, considering that the α surface reacts readily with water [14], affecting its surface reactivity [15], the present study on the UHV κ surface gives valuable insight for studying such effects at metastable-alumina surfaces.

The results show a huge inward relaxation (-117%) of κ-Al_2O_3(001), yielding O termination. This is understood by the open structure of the crystal, caused by the presence of Al^T and by Pauling's third rule. This suggests that strongly relaxed surface Al ions are common in metastable Al_2O_3, explaining the observed presence of abnormally coordinated Al ions in bulk-structure studies of porous aluminas [10]. An instability of surface-layer Al^T is predicted and the importance of long-range electrostatics for surface relaxation is showed. Low crystal symmetry makes all surface terminations of κ-$Al_2O_3(001)/(00\bar{1})$ nominally polar, in Tasker's sense. However, by including effects beyond his point-charge model, we show that the lowest-energy termination is in reality nonpolar. Because of the charge asymmetry inherent in κ-Al_2O_3 and the anisotropy of its Al-sublattice structure, the presence of a one-dimensional (1D) Fermi gas at $(00\bar{1})$ is then predicted.

Bulk α and κ are composed of alternating O and Al planes, perpendicular to the c axis ([0001] in α, [001] in κ), with O in an almost close-packed stacking (*ABAB* for α, *ABAC* for κ) and Al in interstitial sites. In α all Al layers consist of hexagonally arranged atoms, occupying 2/3 of the available Al^O sites. Because of the electrostatic repulsion caused by face sharing of the Al^O in neighboring layers, the Al ions in each layer are separated along [0001], forming two sublayers. All Al layers are equivalent except for an in-plane displacement of the hexagons of one Al^O site in subsequent layers. Thus, the α structure is mirror symmetric through (0001), with the Al sublayers equidistantly distributed around any O layer. In κ only every second Al layer is equivalent (Fig. 1): while every second layer has only Al^O, arranged in close pairs of [100] zigzag lines separated along [001], the other layers are "mixed" (M) and consist of two [100] zigzag lines with only Al^T and Al^O, respectively, that alternate along [010] equidistantly from each other (see Fig. 7 in Ref. [3]). Because of their coordination, the Al^T are strongly displaced in the $[00\overline{1}]$ direction. Also, in each layer the O atoms are separated along [001], due to the Al-sublattice anisotropy. Considering the higher stability of α, Al^O are more stable than Al^T in bulk Al_2O_3, a fact in agreement with Pauling's first rule. Yet, in κ the Al^T presence allows the structure to avoid face sharing between Al coordination polyhedra, thanks to the vacancy lines in the Al^O layer, directly beneath the Al^T. According to Pauling's third rule, this provides stability and is presumably the cause of the high transition temperature to α ($\approx$1000 °C). This stabilizing mechanism appears in other metastable aluminas as well: both the monoclinic θ and the spinels of γ, η, and δ [2,10,11] have Al^T arranged such that Al face sharing is avoided [16]. The lower symmetry of κ implies: (i) inequivalence of $\kappa(001)$ and $(00\overline{1})$, since the fact that all Al^T are aligned in the same direction causes a lack of (001) mirror symmetry; (ii) possibility of twice as many surface terminations for $\kappa(001)/(00\overline{1})$ as for $\alpha(0001)$, due to the presence of two different Al layers in κ; and (iii) Tasker polarity of all κ terminations, due to the unsymmetrical Al-O interlayer distances caused by the lack of mirror symmetry. In contrast, the (0001) mirror symmetry of α implies: (i) equivalence of $\alpha(0001)$ and $(000\overline{1})$ and (ii) existence of a Tasker-nonpolar α termination, that is, with cleavage plane in-between two Al sublayers.

We perform calculations on all ten possible κ surface terminations (Fig. 1), including full relaxation, with the DFT plane-wave code DACAPO 1.30 [17]. PW91 exchange and correlation approximation [18], ultrasoft pseudopotentials [19], slab geometry, and periodic boundary conditions [20] are used. Calculations on the clean nonpolar $\alpha(0001)$ yield surface relaxations of -85%, $+3\%$, -45%, $+20\%$, $+5\%$, -7%, in agreement with Ref. [7]. Optimization of bulk κ yields lattice parameters $a = 4.875$ Å, $b = 8.378$ Å, and $c = 9.018$ Å, $\sim$0.9% larger than experimental room-temperature values [21], and a κ-α bulk-energy difference of 0.089 eV/Al_2O_3, in good agreement with experiments [22] and other theory [11]. A vacuum thickness $L_{vac} = c$, a plane-wave cutoff of 400 eV, and a $4 \times 2 \times 1$ Monkhorst-Pack **k**-point sampling of the Brillouin zone are used for the κ surfaces. The energy of separation, E_{sep} [the sum of (001) and $(00\overline{1})$ surface energies] is calculated as $E_{sep} = E_{cell}(n) - nE_b$, where $E_{cell}(n)$ is the supercell energy for a slab with n repeat units (each with two O layers in κ), and E_b, the bulk energy of one unit, is obtained as $E_b = E_{cell}(n) - E_{cell}(n-1)$ [23]. In the case of a mirror-symmetric slab $E_{sep} = 2E_s$, where E_s is the energy of each of the two equivalent slab surfaces. For a nonsymmetric crystal such as κ-Al_2O_3 only E_{sep} can be calculated. However, E_{sep} is the energy required to cleave the bulk crystal through a given plane and thus the relevant quantity for comparing the stability of different surface terminations. The κ E_b and E_{sep} are well converged at $n = 4$. For the deep $(00\overline{1})$ relaxation thicknesses up to $n = 7$ are used. Full details of calculations and results will be given in a separate paper.

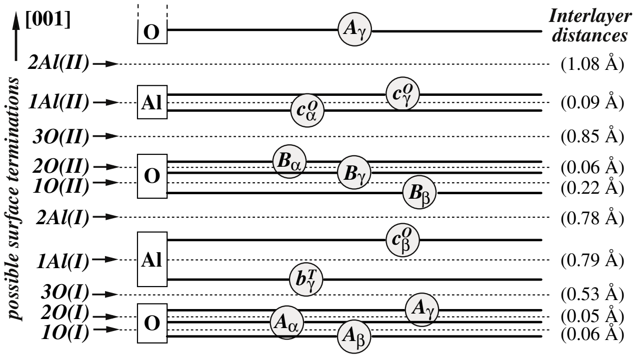

FIG. 1. Atomic layers in bulk κ-Al_2O_3 for half a unit cell (a surface "repeat unit"). The position of each atom can be classified, as indicated by the notations [3]. Roman letters denote stacking letter. Greek subscripts denote the three different ion positions within each layer that, for a given stacking letter, are allowed by the κ-Al_2O_3 space group. Superscript "O" ("T") indicates octahedral (tetrahedral) Al.

The resulting E_{sep} is lowest for 1Al(I), one of the two terminations [1Al(I) and 1Al(II)] most resembling the nonpolar $\alpha(0001)$, with its half-Al-layer termination, but, in contrast to 1Al(II), it lacks Al^T in the immediate subsurface layer. Indeed, relaxation of other terminations with Al^T near the surface shows an instability of these Al^T units in the form of lateral displacements of the surface O (Al) atoms lying directly on top of second-layer Al (O) atoms. However, when a new layer of Al is put above these terminations the Al^T instability disappears. This follows Pauling's rules: the removal of the neighboring Al layers, which in the bulk stabilize the Al^T through the lack of face sharing, exposes the Al^T instability. Since the same Al^T-stabilizing mechanism appears in other metastable aluminas, this surface-Al^T instability should be a general result. The 1Al(I) E_{sep} values are, after (before) relaxation of both (001) and $(00\overline{1})$ faces, 4.0 (7.0) J/m^2, close to our values for the nonpolar $\alpha(0001)$, 3.2 (7.2) J/m^2.

The lack of Al face sharing makes the κ structure more open than α [density = 3.98 (3.77) g/cm^3 for $\alpha(\kappa)$ [24]]. Our calculations show that this causes a dramatic relaxation of κ 1Al(I)(001) (Fig. 2): the vacancy lines right beneath the surface Al allow a -117% contraction of the surface Al-O interlayer distance, yielding an O termination. As for $\alpha(0001)$, which also relaxes strongly [5–8], the relaxation results from the combination of an open structure with the strong electrostatic attraction of surface

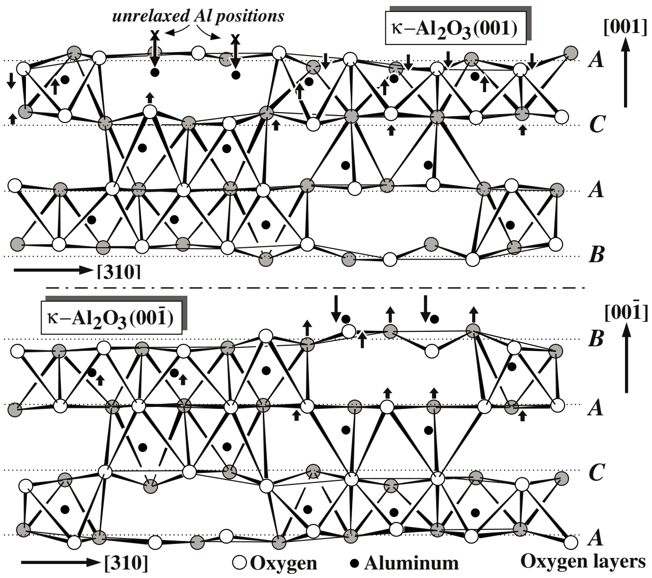

FIG. 2. Relaxation of κ-$Al_2O_3(001)$ and $(00\bar{1})$. A slice of the atomic structure is shown, one coordination-polyhedron thick. "Shaded" O atoms lie behind "open" ones in the same layer. Solid lines show the Al coordination polyhedra. The arrows show the major atomic displacements during relaxation.

Al-O caused by the high ionicity and the lowered coordination of surface Al after the bulk-structure cut. In κ, however, the wider vacancy region in the second Al layer further lowers Pauli and electrostatic repulsions between first- and second-layer Al. The surface Al (b_γ) relax inwards by 0.92 Å to a quasitrihedral site 0.30 and 0.40 Å below the nearest-neighbor (NN) O, A_α, and A_γ, respectively. The open structure allows the giant relaxation with bond lengths intact: the relaxed surface Al-O lengths, 1.73−1.74 Å, are close to bulk Al^T values (1.75−1.79 Å) and the 2.70 Å of the shortest relaxed Al-Al length is not far from the bulk minimum of 2.87 Å. The surface O (A_β) deprived of NN Al (c_β) relax inwards by 0.18 Å, attracted by the subsurface Al^O ($b_\alpha$and b_β), which relax 0.17 Å outwards. This creates [100] troughs in the surface O along the missing Al (c_β) lines. The interlayer distance between the lowest-lying surface O and the former surface Al is 0.09 Å. The relaxation decays rapidly and is smaller than ±0.01 Å from the fourth O layer and on.

This result indicates strong relaxation effects at open metastable-alumina surfaces. Experiments have reported the presence of abnormally coordinated Al in the defect spinel structures proposed for γ and η [10]. However, it has been suggested that these cations actually reside in the surface layer, considering the large surface area of these phases [10]. Our result supports this, since: (i) in analogy to κ, an ideal spinel structure lacks Al face sharing; (ii) DFT studies on spinel Al_2O_3 indicate a preference for Al vacancies at octahedral sites [11]; (iii) an Al vacancy in an octahedral (111) spinel layer creates a large vacancy region for the Al^T directly above to relax into; and (iv) most of the new γ and η surfaces formed during alumina dehydroxylation are (111) [10].

At $(00\bar{1})$, in contrast, the surface Al-O contraction is smaller (−74%). It consists of an inward relaxation (0.39 Å) of the surface Al (c_β) and an outward movement (0.19 Å) of their NN O (B_β). The relaxed bond lengths show that this is not an ideal ionic configuration: the Al-O lengths are short, 1.69−1.75 Å, and the triangle of NN O has expanded (from bulk O-O lengths of 2.79−2.83 Å to 2.85−2.97 Å) to accommodate the Al. This seems to indicate a lower ionic character of this surface. Structurally, there is a subtle difference between (001) and $(00\bar{1})$. In both cases there are vacancies directly beneath the surface Al. However, while in the third layer of (001) the Al beneath the surface Al are Al^O, at $(00\bar{1})$ they are Al^T lying on top of O (Fig. 2). These $(00\bar{1})$ Al^T are thus more constrained in the [001] direction because of Pauli repulsion from the underlying O and exert a stronger electrostatic repulsion on the surface Al than the Al^O of (001). Indeed, the (001) third-layer Al^O relax inwards by 0.04 Å whereas the $(00\bar{1})$ Al^T remain still. The hindered $(00\bar{1})$ surface-Al relaxation then causes the NN surface O to move outwards, in an attempt to minimize the Madelung energy. This has long-ranging effects, causing collective outward O displacements by 0.01−0.02 Å at least as deep as ten layers into the bulk. It is fascinating to notice how these structural subtleties have such crucial importance for the surface stability of an ionic crystal.

Although all $\kappa(001)/(00\bar{1})$ terminations should be polar, in Tasker's sense [13], no sign of $E_{\rm sep}$ divergence with increasing slab thickness is found for 1Al(I). To elucidate this and the above indication of a lower ionicity of 1Al(I) $(00\bar{1})$, we analyze the local density of states. For unrelaxed (UR) 1Al(I), both (001) and $(00\bar{1})$ have metallic surface states (SS), of predominantly s and p_z character, localized on the surface Al and NN O atoms. Like the SS of UR $\alpha(0001)$ (Refs. [5] and our calculations), they stem from the surface-Al dangling bonds caused by the loss of coordination. After relaxation (R), (001) loses its SS but retains the crossing of O valence bands over E_F, whereas $(00\bar{1})$ keeps a partly filled SS. This indicates a charge transfer from (001) to $(00\bar{1})$, which we further investigate by calculating surface atomic charges (Table I) from the DFT densities with the Voronoi approach of Ref. [3]. For both UR and R, the electrons are strongly localized around the O closest to the surface Al [25]. Indeed, cutting of the bulk structure breaks Al-O bonds, causing the electrons donated to these bonds by the Al to be restored to the Al and/or their remaining NN O. At the same time, O ions that lose NN Al are stripped of the electrons donated to them by these Al ions. This electronic give-and-take can be quantified with Brown's valence-sum rule [26], an improvement of Pauling's second rule with more rigorous semiempirical and QM motivations [27] that takes into account the effects of crystal asymmetry. It states that the valence of an atom j is $V_j = \sum_i s_{ij}$, where $s_{ij} = \exp[(r_0 - r_{ij})/B]$ are the bond strengths between atom j and its NN atoms i, r_{ij} are the bond lengths, $B = 0.37$ Å, and $r_0 = 1.651$ Å for Al-O. Use of our DFT

TABLE I. Calculated surface atomic ionicities.

Surface		κ-$Al_2O_3(001)$			κ-$Al_2O_3(00\bar{1})$			
Atom		O		Al	Al		O	
	(A_α)	(A_β)	(A_γ)	(b_γ^T)	(c_β^O)	(B_α)	(B_β)	(B_γ)
Bulk	−1.92	−1.87	−1.90	+2.89	+2.78	−1.80	−1.79	−1.93
UR	−1.84	−1.42	−2.13	+2.87	+2.62	−1.90	−2.22	−1.58
R	−1.80	−1.68	−1.88	+2.88	+2.74	−1.88	−2.05	−1.78

bulk bond lengths yields values of $V = 2.91$ (2.82) for the Al^T (Al^O) of the M Al layer, very close to the bulk ionicities of Table I. Brown's s_{ij} is thus a good measure of the electron charge donated by an Al atom to its NN O. According to it, the charges donated by the Al^T (Al^O) of a bulk M Al layer to the NN O atoms in the layers above and below are 0.69 (1.83) and 2.22 (0.99) electrons, respectively. The asymmetry is due to the Al^T asymmetry and the Al^O distortion. Creation of 1Al(I) surfaces removes then $2 \times (0.99 - 0.69) = 0.6$ electrons/unit cell from (001) and gives them to $(00\bar{1})$. Indeed, summation of the charges of Table I shows (001) and $(00\bar{1})$ to lose and receive, respectively, ~0.6 el/cell compared to the bulk [28]. Is this the charge transfer needed to neutralize the polarity of 1Al(I)? Use of Eq. (4) in Ref. [29], which allows varying ionicities and interlayer distances, with the ionicities of Table I, yields a needed charge transfer of 0.69 el/cell, quite close to our DFT result. However, our analysis shows that this transfer is *not* the result of charge flowing from the (001) to the $(00\bar{1})$ surface of the slab, a picture inconsistent with the high ionicity of bulk Al_2O_3. Rather, we show that Tasker's rules are insufficient in dealing with systems of low symmetry such as κ-Al_2O_3. The polarity is only *apparent,* arising from a point-charge model of the crystal.

The presence of metallic SS on R $(00\bar{1})$ is thus necessary to accommodate the electron excess. At (001) the extra electrons received by O (A_γ) from the undercoordinated surface Al (b_γ) are efficiently redistributed during relaxation to the "undercharged" O (A_β), which have lost their NN Al (c_β), restoring ionicity. At $(00\bar{1})$, however, such redistributions are unable to accommodate the extra electrons, which do not fit into the ionic description. [At the same time, the electron deficit at (001) is seen in lower ionicities for O (A_β and A_α), causing empty states at the top of these O valence bands.] Thus, the $(00\bar{1})$ SS is localized on the surface Al and their NN O, which gives it the character of a pseudo-1D electron gas along the [100] zigzag surface Al line. This is confirmed by the calculated $E(\mathbf{k})$ dispersion, which is parabolic-like along [100] (effective electron mass of $0.14m_e$) and almost flat along [010]. Such a peculiar system should have interesting properties for, e.g., adsorption and catalysis and is currently under investigation.

In conclusion, DFT studies of κ-$Al_2O_3(001)/(00\bar{1})$ show a need to extend Tasker's rules on the stability of presumed polar surfaces to account for low-symmetry effects. The role of Al^T in metastable aluminas is investigated, showing it to cause strong relaxation effects due to the open structure. Also, the presence of Al^T close to the surface is unfavored. Finally, the bulk charge asymmetry introduced by the Al^T and the Al-sublattice anisotropy create a 1D surface electron gas at $(00\bar{1})$.

We thank L. Bengtsson for DACAPO 1.30 support and M. Halvarsson for discussions. Financial support from the Swedish Foundation for Strategic Research via Materials Consortium # 9 and computer use at UNICC, Chalmers, and PDC, KTH, Stockholm are acknowledged.

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