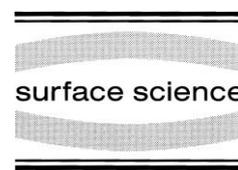




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# The surface structure of $\alpha$ -Al<sub>2</sub>O<sub>3</sub> determined by low-energy electron diffraction: aluminum termination and evidence for anomalously large thermal vibrations

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## Abstract

We have determined the surface structure of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) using dynamical low-energy electron diffraction (LEED). Sapphire surfaces were prepared in three different ways, and the diffraction results were analyzed using an exhaustive search of possible models. For all sample processing conditions, the clearly favored structure has a single aluminum layer termination and a large first interlayer contraction. In addition, we find that the surface atoms have unusually large vibrational amplitudes at room temperature, suggestive of an anharmonic vibrational mode. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Aluminium oxide; Low energy electron diffraction (LEED); Low index single crystal surfaces; Surface relaxation and reconstruction

Being the simplest and only thermodynamically stable aluminum oxide [1],  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is a prototype for understanding metal oxides. Because of its importance, numerous experimental [2–7] and theoretical [8–14] investigations of its surfaces have been performed. Nonetheless, a most basic property of the simplest clean surface, namely the structure of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001), remains controversial.

Compared with monoatomic materials, determining the surface structure of a compound has

additional complicating factors. First, a compound may terminate along different planes, giving inequivalent structures. Three different  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) plane terminations exist: a single aluminum layer (A11), an oxygen layer (O1) and a double aluminum layer (A12) (terminating layers are denoted as labeled in Fig. 1). Theoretical calculations predict that  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) has an A11 termination with a greatly contracted first interlayer spacing ( $\sim 85\%$ ) [8,9,13]. X-ray diffraction [4] and ion-scattering [2] experiments concluded that the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) surface is A11-terminated; however, the models considered in these investigations were limited to the ideal A11, O1 and A12 surfaces.

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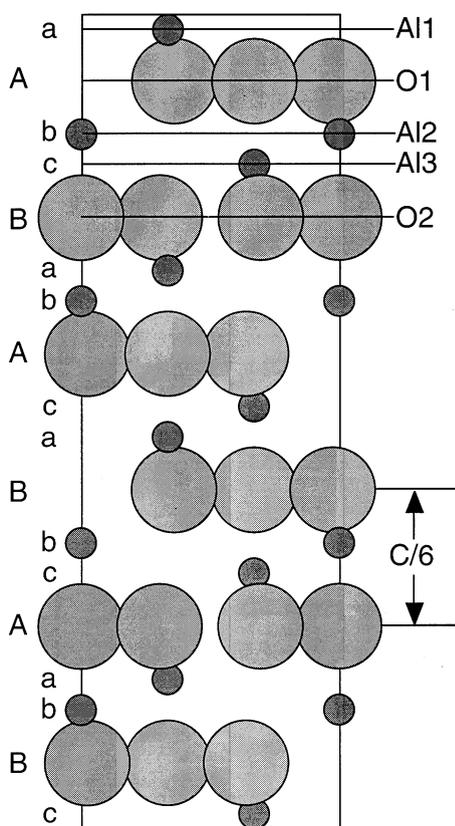


Fig. 1. Illustration of the 12 aluminum layers and the six oxygen layers of the  $\alpha$ - $\text{Al}_2\text{O}_3$  hexagonal unit cell, shown parallel to the (0001) surface. The oxygen layers follow hcp-type stacking (ABAB...), and the aluminum layers follow fcc-type stacking (abcabc...). Oxygen layers separated by  $c/6$  along the  $c$ -axis are equivalent only after a mirror operation, a symmetry operation that does not pertain to the unit cell as a whole.

A further complication is that  $\alpha$ - $\text{Al}_2\text{O}_3(0001)$  can be terminated in such a way that chemically and energetically equivalent, but diffractationally inequivalent, planes exist in the near-surface region (e.g., O1 and O2 planes) [6]. If a sample has a terrace-and-step structure with step heights an odd multiple of  $c/6$  (where  $c$  is the unit-cell height), the diffraction pattern will have contributions from both terrace types.

Additionally, compound surfaces may be phase-separated, i.e., consist of terraces having different stoichiometry or structure, and the existence of a phase-separated surface, and the amounts of each phase, may depend sensitively on processing condi-

tions [8,9,13]. In fact, the previous low-energy electron diffraction (LEED) study on  $\alpha$ - $\text{Al}_2\text{O}_3(0001)$  concluded that a mixture of aluminum- and oxygen-terminated terraces best modeled the data [6]. However, a recent ion-scattering study [5], which also considered a mixed-termination model, concluded that the Al1 model best fit the data.

Finally, the surface of a compound may not be derived from a planar cleavage of the bulk — the near-surface layers may have a different stacking sequence, yet still maintain the observed surface symmetry. Consideration of such structures is particularly relevant for  $\alpha$ - $\text{Al}_2\text{O}_3(0001)$ , where the closely related  $\gamma$ -phase has been suggested to have a lower surface energy [11]. Because of the above complexities, we have studied the  $\alpha$ - $\text{Al}_2\text{O}_3(0001)$  surface structure with particular emphasis on two issues: sensitivity of the surface to sample-preparation effects, and completeness of analysis.

The sapphire crystal was first annealed in air in a high-purity environment (i.e., a sapphire-lined furnace) at  $1425^\circ\text{C}$  for 12 h, which produced a surface with large terraces ( $\sim 1000 \text{ \AA}$ ). It was then sequentially cleaned in acetone, methanol, 1 M HCl and deionized water. Residual carbon contamination was removed in the vacuum chamber using an atomic deuterium beam created by a commercial, neutralized, radio-frequency plasma discharge [15]. To investigate the sensitivity of surface structure to processing conditions, we finished the processing in three very different ways: (1) turn off the atomic deuterium beam and then cool in vacuum ('Vac' data); (2) cool to  $200^\circ\text{C}$  before turning off the atomic deuterium beam ('D' data); and (3) turn off the atomic deuterium beam, heat for 5 min in  $5 \times 10^{-5}$  Torr  $\text{O}_2$ , and then cool in vacuum ('Ox' data). All three procedures produced bright, sharp,  $(1 \times 1)$  LEED patterns with three-fold symmetry. The LEED data were acquired with the sample near room temperature, and nine inequivalent beams were recorded at normal incidence in the energy range of 80 to 370 eV (total range 2080 eV). After subtracting the background, equivalent beams were averaged and the intensity was scaled to the incident electron current.

While bulk  $\alpha$ - $\text{Al}_2\text{O}_3(0001)$  has rhombohedral

symmetry, the atomic positions are usually given in terms of a hexagonal unit cell (Fig. 1). In this unit cell, the 12 aluminum layers are translationally equivalent to each other. For the six oxygen layers, alternate layers are translationally equivalent, and sequential layers are equivalent after a translation and mirroring through a plane perpendicular to the surface. Any of these 18 layers may serve as a surface termination, and each of these surfaces has  $p3$  symmetry and no mirror planes. However, while a surface that terminates in layers {Al1–O1–...} is energetically equivalent to one that terminates in layers {Al3–O2–...}, the mirror-symmetry relationship of the adjacent oxygen layers results in these terminations being diffractationally inequivalent. Therefore, both terminations must be included to correctly model a terraced surface.

The simplest models used to analyze our data were the ideal planar cleavages: models Al1, Al2, Al3, O1 and O2. A related model consisted of an oxygen atom on top of each surface aluminum atom in the Al1 model. Since the scattering power of hydrogen is small enough to be neglected, this model represents a water-covered surface.<sup>1</sup> The next level of complexity involves surfaces that terminate in a single species, i.e., aluminum or oxygen, but contain diffractationally inequivalent terraces: models Al1 + Al3, O1 + O2, Al<sub>m</sub> and O<sub>m</sub>. The subscript 'm' refers to constraining the calculations such that the atoms in the mirrored terraces have the same relative positions.<sup>2</sup> We also considered models having mixtures of terraces that terminated in different species. Five models with variable mix ratios were examined: Al1 + O1, Al1 + O2, O1 + Al3, O1 + Al2 and (Al<sub>m</sub>) + (O<sub>m</sub>). However, to limit the number of adjustable parameters in the last model, we constrained the mirror-related terraces to have equal abundance, but allowed a variable mix between the species.

The above models all represent cleavage(s) of the bulk structure, in which the oxygen and alumi-

num layers follow hexagonal close-packed (hcp) type stacking (ABAB...) and face-centered cubic (fcc) type stacking (abcabc...), respectively (Fig. 1). We also considered the five stacking-fault models involving shifts of the outermost aluminum or oxygen layer that preserved the observed surface symmetry.

Finally, we have considered the possibility that the surface aluminum atoms in the theoretically favored Al1 model have anisotropic vibrations that cannot be correctly described by the isotropic Debye–Waller approximation used in the calculation. If this is the case, the Al1 model will result in a poor fit to the data even if the surface is in fact terminated by a single aluminum layer. To investigate this possibility, we modeled the surface with a 'split atom' [16–18] by constructing an equal mixture of two identical domains that are allowed to relax independently.

The LEED analysis applied familiar methods, specifically the symmetrized automated tensor LEED [19] used, for instance, in the study of Fe<sub>3</sub>O<sub>4</sub>(111) [20,21]. One additional criterion, known in X-ray crystallography as the Hamilton-ratio test [22,23], is herein introduced to LEED to deal with variable numbers of fit parameters, as occurs when comparing a single structure with a mix of structures. The Hamilton ratio helps to distinguish real improvements in a fit due to choosing a better model from artificial improvements due only to fitting more structural parameters. A large ratio is indicative of real improvements (as long as the structural coordinates are otherwise reasonable).<sup>3</sup> In all of the models we tested, the

<sup>3</sup> The Hamiltonian ratio, modified to the LEED case, is defined as

$$H_r = \frac{(R_s^2 - R_{\text{mix}}^2)(n - p)}{R_{\text{mix}}^2(p - q)},$$

where  $R_s$  and  $R_{\text{mix}}$  are the  $R$ -factors for the model with the smaller ( $q$ ) and larger ( $p$ ) number of fitting parameters. In a beam intensity as a function of voltage spectrum [ $I(V)$ ], the width of the dominant peak is about  $2|V_{\text{oi}}|$ , where  $V_{\text{oi}}$  is the inner potential. In addition, the  $I(V)$  curves usually contain as many peaks as can possibly be fit into the available energy range. Therefore we assume that  $n$ , the number of diffraction peaks, is reasonably estimated by the total energy range divided by the peak width. In our experience this formulation is applicable to all the various  $R$ -factors commonly used in LEED, and the ratio should exceed 3 to indicate real improvements.

<sup>1</sup> A recent X-ray diffraction study concluded that the hydrated  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) surface is oxygen-terminated [7]. Since we also considered essentially this model (O1) and found it to be unacceptable, we conclude that our surface was not hydrated.

<sup>2</sup> In all cases where mixed domains were considered, the calculated spectra were derived from incoherently summing over the two terraces.

Table 1

$R_p$ ,  $H_r$  and the change in the first two interlayer spacings (with representative uncertainties) for the best fits to models All + O1 and All-split, for the three sample preparations. For All-split, and the aluminum domains of the All + O1 models,  $\Delta d_{12}$  is the Al1–O1 spacing (averaged for All-split) and  $\Delta d_{23}$  is the O1–Al2 spacing (averaged for All-split). For the oxygen domain of the All + O1 model,  $\Delta d_{12}$  is the O1–Al2 spacing, and  $\Delta d_{23}$  is the Al2–Al3 spacing. Also shown are the changes in the first two interlayer distances provided by X-ray diffraction and theory

	$R_p$	$H_r$	$\Delta d_{12}$ (%)	$\Delta d_{23}$ (%)
All + O1 (Ox)	0.33	3.58		
Al domain			+5.0 ± 8.0	+0.2 ± 7.0
O domain			+2.4	–11.8
All + O1 (Vac)	0.33	3.03		
Al domain			0.0	+5.0
O domain			–1.7	–14.8
All + O1 (D)	0.32	3.96		
Al domain			–38.4	+7.5
O domain			0.0	–20.2
All-split (Ox)	0.30	4.13	–52.8 ± 5.0	+1.5 ± 5.0
All-split (Vac)	0.29	3.88	–50.0	+6.3
All-split (D)	0.29	4.55	–50.6	+5.8
X-ray [4]			–50.8	+16.0
Theory [14]			–87.4	+3.1

atoms were allowed to fully relax down to a depth of seven layers under the provision that they maintain the observed  $p3$  symmetry.

For each of the different sample preparations, we have examined 21 different surface models within six model classes — the most exhaustive structural examination of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) performed to date. The results of the optimized fitting of the models are summarized in Fig. 2. We look for structures with low Pendry  $R$ -factors ( $R_p$ ), preferably lower by 20% than other structures, and relatively large Hamilton ratios ( $H_r$ ). Additionally, consideration of the atomic positions in the fully relaxed structure will exclude certain structures (Fig. 2).<sup>4</sup> From the above considerations, the split-atom (All-split) and All + O1 mixed-termination models are favored over the

<sup>4</sup> Although the All + O2 and O2 + Al3 models (numbered 17 and 18, respectively) have acceptable  $R_p$ s and  $H_r$ s, their final configurations are close to that of the optimized All + O1 model. Therefore, we discuss only the All + O1 model.

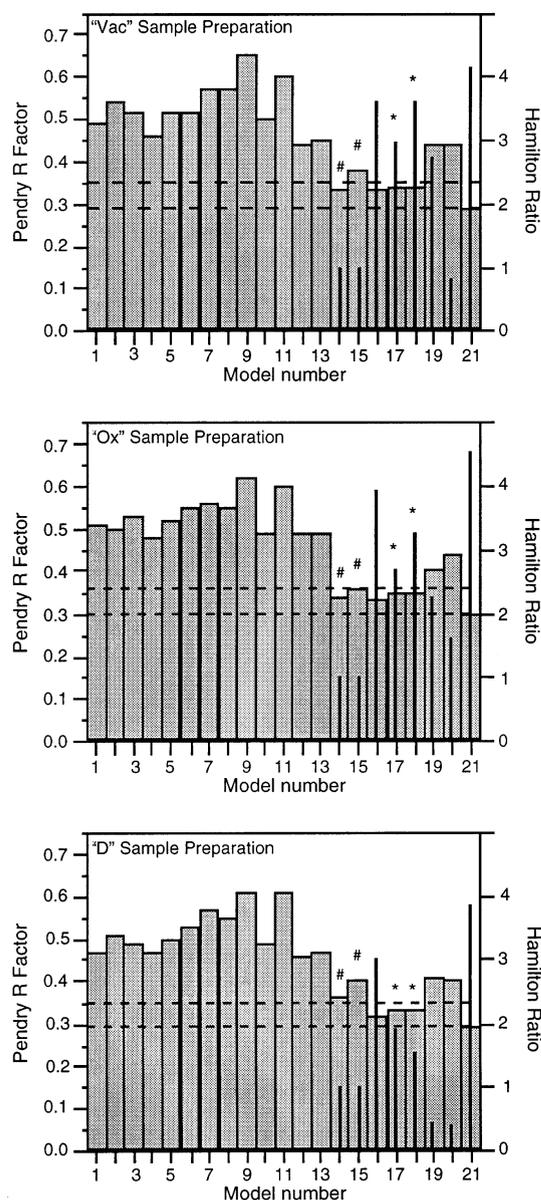


Fig. 2. Pendry  $R$ -factors ( $R_p$ ) (bars) and Hamilton ratios ( $H_r$ ) (lines) for the three  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) sample-preparation methods and the 21 models tested. The horizontal lines bracket the range within 20% of the best  $R_p$  value. The models are numbered along the horizontal axis as: 1–5, ideal (0001) terminations; 6, water-covered surface; 7–11, stacking faults; 12–15, single-species mirrored surfaces; 16–20, mixed-species terminations; and 21, split-atom model. The stars in the figure denote models whose optimized structures are close to those of the All + O1 model, despite the fact that the starting configurations were very different. The hash signs in the figure denote models that resulted in large, non-physical bond lengths (e.g., a top-layer expansion of 90%).

other models, irrespective of the surface preparation. Table 1 lists the  $R_p$ s and the change in the first two interlayer spacings (with respect to the bulk spacing) for the best fits to these models, for all three preparation methods. Additionally, the change in the first two interlayer spacings is given for a prior X-ray experiment and a theoretical calculation. Clearly, the Al1-split model has the lowest  $R_p$ s and the highest  $H_i$ s. However, since the Al1+O1 model has acceptable  $H_i$ s and  $R_p$ s that are only  $\sim 10\%$  greater, this model cannot be immediately discarded.

The best-fit Al1+O1 model has several questionable properties. First, fitting the two ‘cleanest’ preparation methods (Ox and Vac) with the model gave surfaces that are essentially bulk-like, while the deuterium-exposed preparation (D data) produced a significant first-interlayer contraction (Fig. 3). This is counter to the usual expectation that clean surfaces are contracted and that adsorption of hydrogen results in a first-interlayer spacing close to the bulk value [24,25]. Second, the Al1+O1 models were very insensitive to the relative amounts of aluminum and oxygen terraces,

with the uncertainty in the mix ratio being about  $\pm 30\%$  for all three preparations. Finally, the Al1+O1 model is inconsistent with theoretical calculations, which preclude a phase-separated system [8,9,13].

In contrast, for all three sample preparations, the simpler Al1-split model gives consistent and physically reasonable results. The only significant difference in the position of the atoms in the two terraces is in the top aluminum layer. This supports the validity of the model — if the positions of the atoms in the other layers differed, it would indicate that the fit was being optimized by a non-physical utilization of these additional degrees of freedom. In the split-atom method, the difference in the position of the atoms in the domains is related to their vibrational amplitude. The large difference we observe, about  $0.24 \text{ \AA}$ , is indicative of an anharmonic enhancement of the perpendicular vibrational mode of the outermost aluminum atoms. Additionally, the first-interlayer spacing (derived from the average of the two domains) is in reasonable agreement with the previous X-ray measurement [4]. While we find a large interlayer

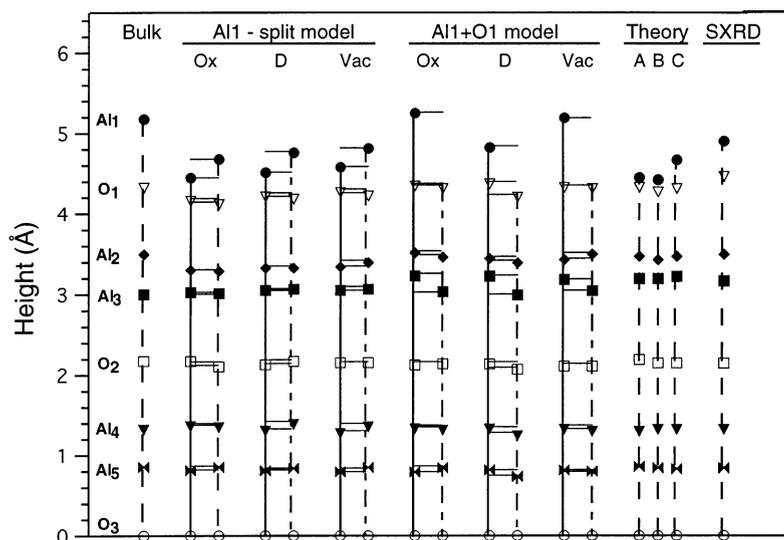


Fig. 3. Graphical representation of the atomic positions in both terminations for the Al1-split and Al1+O1 models, compared with the bulk and results from theory (A, Ref. [14]; B, Ref. [12]; and C, Ref. [10]) and X-ray diffraction [4]. Each vertical line represents one termination and gives the optimized height of each atomic layer (labeled by individual symbols) above the first fixed oxygen layer (height =  $0 \text{ \AA}$ ). Pairs of connected lines correspond to pairs of terminations that were optimized together, showing resulting height differences.

contraction at the surface, it is significantly smaller than that predicted from state-of-the-art calculations [8,9,13]. Harrison et al. have suggested that this discrepancy results from the failure of the zero-temperature calculations to account for large surface vibrations [26]. In general, surface atoms have vibrations about 30–40% larger than those in the bulk, yet our results suggest a vibrational amplitude approximately 100% greater than the bulk value at room temperature.<sup>5</sup> While surprising, this result is not without precedent — large vibrations have been observed on metal surfaces [27–29], and have also been predicted, but not yet detected, for other oxides [26]. Such large vibrations may have important implications for understanding the surface properties of metal oxides. In the sapphire case, the presence of enhanced vibrations at the surface is easily visualized in terms of the reduced coordination. The Al–O bonds of the surface aluminum atoms are almost parallel to the surface. Thus the vibrations are primarily governed by bond angle changes, which are generally softer than bond length changes. Finally, the fact that our three sample-preparation methods result in the same structure implies that the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) surface is very stable.

In summary, we have studied the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) surface structure by examining an unprecedented number of model structures and emphasizing the sensitivity to the sample-preparation method. We conclude that the surface termination of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) is a single aluminum layer, that the first interlayer spacing is significantly contracted with respect to the bulk spacing, and that the surface structure is insensitive to our different processing methods. Also, we have determined that the topmost aluminum layer has an unusually large vibrational amplitude at room temperature. Such vibrations may account for the substantial difference between the interlayer contractions determined by zero-temperature calculations and finite-temperature experiments.

<sup>5</sup> Using the Debye temperature for the aluminum atoms derived from the LEED calculations (350 K), we calculate a bulk vibrational amplitude of 0.12 Å at room temperature.

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