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## Structure of the (001) surface of $\gamma$ alumina

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Using density functional theory, we have studied the structure and energetics of the (001) face of  $\gamma$  alumina. Our results address several experimental issues: (1) When the face with tetrahedral aluminum is exposed in the bulk-terminated system, the surface reconstructs extensively, leading to exposure of the higher-density layer. When only a few layers are present, this reconstruction may even lead to the collapse of the system into a different structure. (2) We find that the lowest energy is obtained if the vacant spinel sites lie on octahedral positions. We also find that vacancies are less preferred on the surface than in the bulk. (3) Migration to and from the surface of vacant spinel sites, by hopping of Al atoms between octahedral and tetrahedral cation sites has a rather high barrier. This suggests the vacancy distribution may not reach equilibrium if the material is not annealed carefully during preparation. © 2002 American Institute of Physics. [DOI: 10.1063/1.1496469]

### I. INTRODUCTION

Aluminum oxide (alumina) has many uses in ceramics, abrasives, refractives, membranes, and chromatography and as an adsorbent, catalyst, and catalytic support. The latter three uses depend on the properties of the surface. In this article, we use density functional theory to study the structure of the (001) surface of  $\gamma$  alumina. The bulk structure of  $\gamma$  alumina is closely related to that of magnesium spinel ( $\text{MgO}, \text{Al}_2\text{O}_3$ ).<sup>1</sup> Figure 1 shows the spinel unit cell, with the  $z$  axis in the (001) direction. A spinel has 24 cations (Mg or Al) and 32 oxygen atoms in the unit cell of a cubic lattice. The atoms in the unit cell are distributed in four high-density layers and four low-density layers, which alternate along the  $z$  direction. The cations in the low-density layer are tetrahedrally coordinated, whereas the high-density layer contains the octahedrally coordinated cations, and the oxygen atoms. The oxygen atoms form a face-centered cubic (fcc) lattice. The magnesium atoms occupy tetrahedral ( $T$ ) sites and the aluminum atoms occupy octahedral ( $O$ ) sites.

$\gamma$  alumina has a spinel structure with Al cations occupying the Al and Mg sites. Because aluminum is trivalent and magnesium is divalent, the number of Al atoms in the spinel structure of  $\gamma$  alumina is smaller than the number of cations (Al and Mg) in the spinel. This means that to reach the proper stoichiometry some of the cation lattice sites in the spinel structure must be empty. The purpose of this article is to study the structure of the (001) surface of  $\gamma$  alumina and the distribution and the mobility of the vacant spinel sites (VSS) at and near the surface. The structure of the surface and the presence of such vacant sites may affect the catalytic properties of  $\text{Al}_2\text{O}_3$  and its properties as a support.

The distribution of VSS in bulk  $\gamma$  alumina is still debated. Neither experiment<sup>2-18</sup> nor theory<sup>1,13,19-27</sup> have reached definite conclusions. There is a consensus that the VSS are randomly distributed,<sup>1,19-27</sup> but there is no agreement regarding their specific location. X-ray diffraction (XRD),<sup>2-4</sup> nuclear magnetic resonance (NMR),<sup>5</sup> transmission electron diffraction,<sup>18</sup> high-resolution transmission elec-

tron microscopy (HRTEM) and selected-area electron diffraction<sup>6,7</sup> results have all been interpreted as evidence that VSS reside mainly in O cation positions. Other XRD,<sup>8</sup> electron diffraction,<sup>9,10</sup> and NMR studies<sup>11-14</sup> suggested a preference for T positions. Based on a NMR experiment and computations, Lee *et al.*<sup>13</sup> have recently proposed a disordered structure having 60% of the VSS at the T sites and 40% at the O sites. Finally, NMR experiments<sup>11,12</sup> have reported the existence of five-coordinated aluminum in  $\gamma$  alumina. We also note that there are several reports of hydrogen in the bulk of  $\gamma$  alumina,<sup>4,22,28,29</sup> which might affect the VSS distribution.

Theoretical studies also reach conflicting conclusions. Mo *et al.*<sup>19</sup> investigated the structure of nonstoichiometric bulk  $\text{Al}_{21}\text{O}_{32}$  (considered an approximation to  $\gamma$  alumina), using an empirical pair potential with fixed formal charges on the cations and anions, and found that the vacancies preferred O sites. According to these calculations, the energy required to move a VSS from an O to a T site is 3.7 eV. Using a different pair potential and molecular dynamics simulations, Alvarez *et al.*<sup>20,21</sup> found, at room temperature, a preference for T vacancies and observed migration of Al atoms from T to O positions during the simulation. Clearly, the conclusions depend on the potentials used and their accuracy is very hard to assess.

Streitz and Mintmire<sup>1</sup> have recently attempted to model the free energy, as a function of temperature, of the various possible configurations of bulk  $\gamma$  alumina. To do this, they used an empirical potential with variable charges. They studied a large ensemble of vacancy arrangements and calculated the average energy as a function of the T occupation ratio. They found that the O vacancies have lower potential energy, but only by 0.53 eV per vacancy. The entropy in these calculations was estimated using a lattice gas model. It is entropically favorable to have a mixture of O and T vacant sites, and at high temperature the fraction of T VSS is about 0.15. If one assumes that this ratio remains fixed upon cooling, one concludes that  $\gamma$  alumina has a sizable fraction of T VSS.

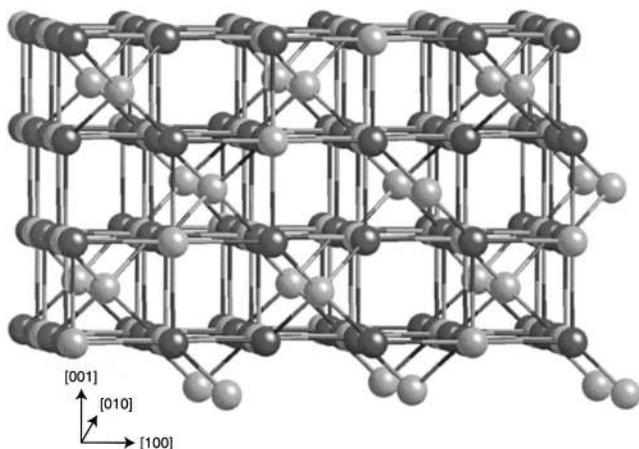


FIG. 1. Schematic representation of a spinel structure with an (001) surface.

Even less is known about the surface structure of  $\gamma$  alumina, in spite of a number of experimental<sup>17,30–37</sup> and theoretical<sup>24,25,38–41</sup> studies. It is generally believed that the termination of the alumina crystallites occurs along a limited number of low-index crystal planes (111), (110), and (100). This hypothesis, which is primarily based on the ion density of various planes and on the likelihood of low index faces, is supported by HRTEM data.<sup>42</sup> An important issue here is the distribution of Al atoms on the surface and their coordination states. Coordinatively unsaturated surface Al atoms are the source of the surface Lewis acidity, which is central to the catalytic activity of the oxide.<sup>17</sup> Prior studies<sup>17,24,25,31–41</sup> have suggested the presence of 3-, 4-, and 5-coordinated Al atoms on the surface, although <sup>27</sup>Al NMR studies<sup>34,35</sup> could observe only 4- and 5-coordinated Al atoms.

Sohlberg *et al.*<sup>24</sup> have recently offered a theoretical justification for the dearth of 3-coordinated Al atoms on the (110C) surface. They reported a massive spontaneous reconstruction of the surface. It is also logical to expect some of the VSS, imposed by the  $\text{Al}_2\text{O}_3$  stoichiometry, to be present in the surface layer of  $\gamma$  alumina.

In this article, we use density functional theory to examine the structure of the (001) face of  $\gamma$  alumina. We look at two kinds of (001) faces, one terminated with the high-density plane, and another terminated with the low-density plane. We have also examined an extremely thin  $\text{Al}_2\text{O}_3$  layer and found that it has a completely different structure than the spinel.

We find that the high-density surface relaxes but does not reconstruct significantly. On the other hand, in the low-density case, a massive reconstruction takes place, which eventually creates a dense surface layer.

We found the following rules for the distribution of the VSS near and at the surface: (1) When a high-density surface is exposed, the VSS prefers to be in the subsurface layers, not in the outermost one; (2) VSS prefer O sites over T sites by 2–3 eV; (3) VSSs have a short-range repulsion that causes them to prefer a fairly uniform distribution within  $\gamma$  alumina.

We have also calculated the activation energy for moving a VSS between a O site and a T site, and we found it to be rather high. This means that the VSS is mobile only at

very high temperature. The distribution in the oxide at lower temperature is likely to depend on the manner in which the material was cooled during preparation. Rapid cooling will freeze in the VSS distribution created during synthesis.

## II. METHOD OF COMPUTATION

Our DFT calculations use a plane wave basis set and ultrasoft pseudopotentials as implemented in the VASP program written by Kresse, Fürthmüller, and Hafner.<sup>43–46</sup> These pseudopotentials were generated according to the scheme outlined by Rappe *et al.*<sup>47</sup> We used the generalized gradient approximation of Perdew and Wang.<sup>48</sup> The energy minimization was carried out using the RMM-DIIS technique<sup>49</sup> and the Pulay quasi-Newton scheme.<sup>50</sup> A 396 eV cutoff was chosen for storage of the Kohn–Sham eigenstates, while a grid of  $80 \times 80 \times 180$  points was used for storage of the charge density. Tests were made to check the convergence with respect to the cutoff and the grid. To aid convergence, a finite temperature approach was adopted where the Fermi function was expanded in a set of orthonormal Gaussian functions according to the method of Methfessel and Paxton.<sup>51</sup> Because the unit cell is very large, the Brillouin zone was sampled using two points in the irreducible wedge.

## III. RESULTS AND DISCUSSION

### A. Simulation cell optimization for bulk $\gamma$ -alumina

Some care must be taken when optimizing the cell volume for  $\gamma$  alumina. The spinel has eight VSS per three unit cells. If the vacant sites are randomly distributed the bulk structure will be cubic, on a large scale. However, in any single calculation, some particular arrangement of VSS in the unit cell must be selected, which breaks the cubic symmetry; so the optimized lattice vectors will not be orthogonal.

Therefore, we have calculated the cell volume indirectly. We carried out two independent calculations of a single spinel cell with two and three cation VSS, respectively. As expected, neither cell was exactly cubic, and they had different volumes. We took the weighted average of the two volumes to reflect the fact that  $\gamma$  alumina has, on average, 2 2/3 VSS per unit cell, and this number will determine the long-range lattice constant. Since the material is cubic at long range, the lattice vectors are orthogonal and equal in length; therefore the lattice constant is the cube root of the weighted-average volume. We obtained a lattice constant of 7.97 Å; the experimental value is 7.90 Å.<sup>6</sup> This length was held fixed in all subsequent surface calculations.

### B. Exposed (001) faces and VSS distribution in $\gamma$ alumina

We start with a spinel structure with cation vacancies on either O or T sites, and either the high or low-density faces of the (001) surface exposed. Most calculations involved simulating a system with a single surface by fixing the atoms in the two lowest layers in their bulk positions. In the other

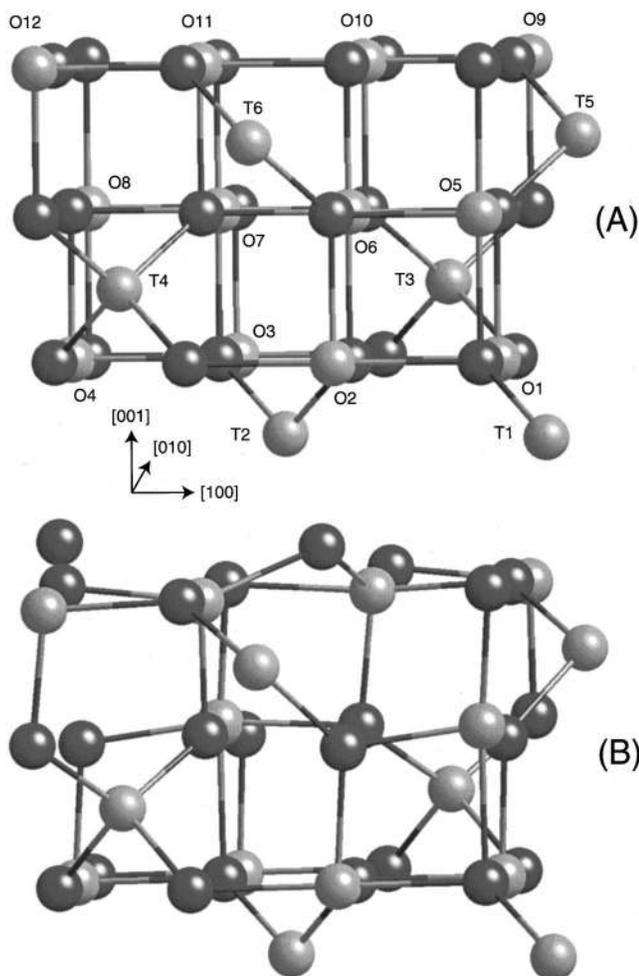


FIG. 2. Schematic representation of  $3/4$  of a spinel unit cell of the  $\gamma$ -alumina structure with a high-density (001) face exposed. Periodicity along the  $x$  and  $y$  axes is evident. The locations of octahedral (O) and tetrahedral (T) cation sites are explicitly shown. (b) Lowest-energy optimized structure obtained for six layers of  $\gamma$  alumina, having vacant spinel sites at positions O6 and O8.

calculations, we simulated a system with two free surfaces, so no atoms were held fixed. The latter calculations are discussed in detail below.

We use three model systems: (1)  $3/4$  of a spinel unit cell (six layers), (2) one spinel unit cell (eight layers), and (3)  $3/2$  of a spinel unit cell (twelve layers). System (1) contains 24 oxygen atoms and 18 cation sites, and so two must be vacant to match the  $\text{Al}_2\text{O}_3$  stoichiometry. System (2) has 32 oxygen atoms and we cannot match the stoichiometry precisely, so we use either 21 or 22 Al atoms (three or two VSS). System (3) has 48 oxygen atoms and four VSS.

Figure 2(a), shows six layers of a  $\gamma$ -alumina slab with a high-density (001) plane uppermost. All 18 cation sites are shown in Fig. 2(a).

With the low-density face exposed, the surface relaxes substantially, and the six-layer system may artificially confine this relaxation. We have found that the twelve-layer calculations allow this relaxation to propagate into the bulk as far as necessary. With the high-density layer exposed, little relaxation occurs and therefore for most calculations we used

TABLE I. Relative energies for various vacant spinel site (VSS) arrangements in  $\gamma$ -alumina ( $3/4$  of a spinel unit cell, two VSS). The lowest energy configuration is used as the zero of energy. The numbering scheme in the left column refers to the cation site labeling in Fig. 1. Configurations with both VSS in the movable layers are shown.

Vacant sites	Energy (eV)
(O6,O8)	0.00
(O6,O12)	0.53
(O6,O11)	1.07
(T5,T6)	2.47
(T4,T5)	3.21
(T3,O12)	3.55
(T3,T4)	4.01

the six-layer system, using the eight- and twelve-layer systems for comparison.

### 1. Exposed high-density face

Because one of the issues in the previous literature is the preference, if any, for O vs T cation sites to be vacant, and because the present simulations involve two vacancies, we have performed three sets of calculations, spanning the three options available to us: both vacancies O, both T, or one O and one T. Within each of these, we have tried various detailed vacancy arrangements.

Figure 2(a) shows how we label the 18 cationic sites to describe which cation sites are vacant in the six-layer calculations. The individual systems are as follows. Both vacancies O: vacant sites are (O2,O6), (O2,O8), (O2,O12), (O6,O8), (O6,O11), and (O6,O12). Both vacancies T: vacant sites are (T3,T4), (T4,T5), and (T5,T6). One O and one T vacancy: vacant sites are (O2,T5) and (O12,T3). The optimized (O6,O8) structure is shown in Fig. 2(b).

The relative energies of the resulting optimized geometries are sorted into two groups, and listed in Tables I and II. Table I shows the energies of those configurations with no VSS in the third (frozen) layer, and Table II the energies of those configurations where one VSS is in the third layer, at (O2) in particular. The energy zeroes of the two tables are set to the optimal configuration in each group.

Since the Al atom at O2, if it is present, is held fixed, and so are all the atoms in that layer, only the atoms above are able to relax in response to the presence or absence of an Al atom at O2. This limited relaxation means that the systems with a VSS at O2 cannot reliably be compared to those without. However, the various calculations in the O2 set can safely be compared among themselves, as they indicate where the other VSS prefers to be.

TABLE II. Same as Table I, but where one of the VSS O2 is in the fixed layer. The energy zero is set to that of the lowest-energy configuration in this class.

Vacant sites	Energy (eV)
(O2,O8)	0.00
(O2,O6)	1.84
(O2,O12)	2.85
(O2,T5)	3.28

We now examine the dependence of energy on the VSS positions. This will answer several obvious questions: (1) Are octahedral or tetrahedral sites favored? (2) Do the VSS prefer to sit in the surface layer or deeper in the slab? (3) Do the VSS interact, is the interaction attractive or repulsive, and what is its length scale? (4) Do the VSS prefer to be in the same atomic layer or in different layers?

The energies in Table I show that the (O,O) pairs have lower energy than the (O,T) and (T,T) pairs. For both (O,T) and (T,T) pairs, the energy is greater than the corresponding (O,O) pairs by 2.5–4.0 eV. The (T,T) arrangements also lie 2.5–4.0 eV above the (O,O) pairs, which is less than twice the amount of moving one octahedral VSS to a T site.

The above energies are in some cases a mixture of various effects; the (O,T) pair (O12,T3) has one VSS on the surface, and thus any surface-bulk preference would be included in its energy. Comparing this with (O6,O12), which also has one surface VSS, gives an energy difference of 3.0 eV to move a VSS from O6 to T3 while the other remains at O12; thus the surface-bulk preference (question 2 above) is disentangled from the octahedral–tetrahedral preference (question 1).

Let us now consider the structures with (O,O) VSS configurations: (O6,O8), (O6,O12), and (O6,O11). (O6,O12) and (O6,O11) have a VSS in the topmost layer. When we move the VSS from the bulk region, O8, to the surface layer (O11) and (O12), we find that the energy increases by 0.5–1.0 eV (see Table I).

We also find that it is unfavorable to have the VSS close together. More specifically, we can define the two VSSs in our calculation to be “neighboring” if at least one oxygen is missing two Al neighbors. In Table I, (O6,O11) has neighboring VSS in this sense. This arrangement is otherwise identical to (O6,O12), which does not have neighboring VSS. The neighboring VSS increases the energy by 0.5 eV between (O6,O11) and (O6,O12).

We now turn to the calculations which had one VSS (at O2) in the frozen layer (see Table II).

Concerning question (1) about O or T sites being preferred by VSS, we note that (O2,T5) differs from (O2,O8) by moving a VSS from O8 to T5, and the energy increases by 3.3 eV. In addition, in comparing these two cases, no VSS lies on the surface, and so we have further proof that the surface-bulk effect is not confusing the octahedral–tetrahedral issue.

The preference of the VSS for the bulk is also confirmed when one VSS is at O2. Comparing VSS arrangements (O2,O8) and (O2,O12), the energy increases by 2.9 eV when a VSS is moved to the surface. This is substantially larger than the difference between (O6,O8) and (O6,O12) mentioned above, 0.5 eV. In both cases, the energy increased upon moving a VSS from the bulk to the surface, but by amounts that differ by 2.5 eV.

The results with a VSS at O2 therefore confirm the repulsion of the VSS from the surface, and also shed light on the physical difference between the two pairs of calculations, which is that the (O6,O8) option has the VSS in the same layer. The VSS at O6 and O8 do not share any oxygen atoms, so they are not neighboring in the sense defined above, but

TABLE III. Same as Table I, but for a full spinel unit cell, with 2 or 3 VSS. The VSS are on octahedral sites in the high-density layers indicated, counting layers down from the surface; there are four such layers. The VSS are placed so as not to share any oxygen atom. Only systems having the same number of atoms can be compared; the zeroes of energy are set to the optimal arrangements within each group.

Layers with a VSS	Energy (eV)
2,3	0.00
1,3	3.19
2,3,4	0.00
1,3,4	1.71

putting both VSS in one layer makes a very uneven distribution of metal-rich and oxygen-rich regions in the  $\gamma$ -alumina system.

If the effect of having one VSS in the frozen layer is not too large, this would indicate that there is a substantial energy penalty for having an uneven VSS distribution. The absolute energies of (O2,O12) and (O6,O12) (which do not appear in Tables I and II because they have different energy zeroes) differ by only 0.14 eV. Their VSS arrangements differ in moving a VSS from O2 to O6, i.e., from the frozen layer to a movable bulk layer. Since neither arrangement has neighboring VSS and both have one surface VSS, this appears to show that the energy gain due to relaxation of the atoms around the VSS is rather modest compared to the energies having a true physical origin in the VSS interactions in  $\gamma$  alumina.

We now consider the eight- and twelve-layer calculations. We have done relatively few calculations, to test the conclusions from the array of six-layer calculations.

In the eight-layer calculations, we have studied four systems (see Table III). These systems have two or three VSS; all VSSs occur on octahedral sites and are as evenly spaced as possible. No two lie in the same layer, and no two share an oxygen.

These systems allow us to compare a VSS in the bulk to one on the surface. As in the six-layer systems, energy is required to move a VSS from bulk to surface. With no VSS in the lowest layer, the energy cost of a surface VSS is 3.19 eV; with a VSS in the lowest layer, the energy cost is 1.71 eV.

The difference between these two energies, about 1.5 eV, gives a measure of VSS interaction. Having a VSS in the fourth high-density layer, even though it is not a neighbor of the third-layer VSS, destabilizes the pair of VSS in the second and third layers, so that moving the second-layer VSS up to the surface does not incur as large an energy penalty as if no VSS had been in the fourth layer. This is evidence that the VSS repel each other even if they are not so close as to share an oxygen, and therefore tend to be as evenly spaced as possible.

Table IV shows the energies of three twelve-layer systems. In these systems, we do not hold the lowest two layers fixed, since the intent here is to simulate a thin film of  $\gamma$  alumina. This idea will be discussed, but we can also comment on the VSS interactions since the reconstruction of the

TABLE IV. Same as Table III, but for 3/2 spinel unit cell, with 4 VSS. The zero of energy is set to the optimal arrangement. Here there are six high-density layers. The VSS in layers 4 and 5 are the same in all calculations.

Layers with a VSS	Energy (eV)
2,3,4,5	0.00
1,3,4,5	2.59
1,2,4,5	4.86

lowest region (i.e., that having the low-density face exposed) does not propagate far into the bulk.

The systems studied correspond to moving two VSS around in the upper three high-density layers. As before, the energy is lowest when no VSS occupies the surface. The next lowest energy, 2.6 eV, involves moving the second-layer VSS up to the surface. This value is typical of the surface-bulk energy differences found in other cases. Moving the third-layer VSS up to the second layer involves a further energy cost of 2.3 eV. Since the closeness of the VSS pairs does not change, this extra energy to move a second VSS close to the surface indicates that the surface VSS repels other nearby VSS more strongly than does a bulk VSS.

To summarize, we have found the following trends. (1) The VSS prefers to occupy octahedral sites over tetrahedral: starting with two O VSS, it costs 2.5–4.0 eV to move one of them to a T site, but no noticeable further penalty to move the other to a T site as well. This nonlinearity indicates substantial interaction among the VSS. (2) Moving an octahedral VSS from bulk to surface costs about 2.5–3.0 eV. Apparently, this happens because the greater number of atoms around the bulk VSS can relax to achieve a lower energy than is available when the VSS lies on the surface. (3) An even distribution of VSS is preferred to an uneven distribution. Of course this really means an uneven distribution of metal-poor oxygens, but the excess energy of an uneven distribution appears as a repulsion between VSS. There are many types of unevenness; considering the possible distributions of two VSS among 18 cation sites gives energies in the range 0.5–2.5 eV. An “uneven” distribution in this context might mean that two VSSs share an oxygen atom, but studies in the larger systems reveal that this repulsion is long ranged: VSS separated by 4 Å (half a spinel unit cell) interact (i.e., determine each others’ preferred sites) with energies of 1.5–2.5 eV. Since the average VSS density in  $\gamma$  alumina is 2 2/3 per spinel unit cell, interactions among VSSs would be strong and could easily affect the surface chemistry of  $\gamma$  alumina.

How safe are these conclusions? It depends how one estimates the error. In many calculations<sup>52–54</sup> where the error could be determined by comparison with the experiment, it has been found that the error of DFT, when computing energy differences, is of the order of 0.2 eV. If the error made is systematic and increases with the number of atoms or bonds in the system, we should be cautious, since this system has a very large number of atoms in the unit cell. However, taking into account the existing experience with DFT calculations, we believe that these conclusions are reasonable.

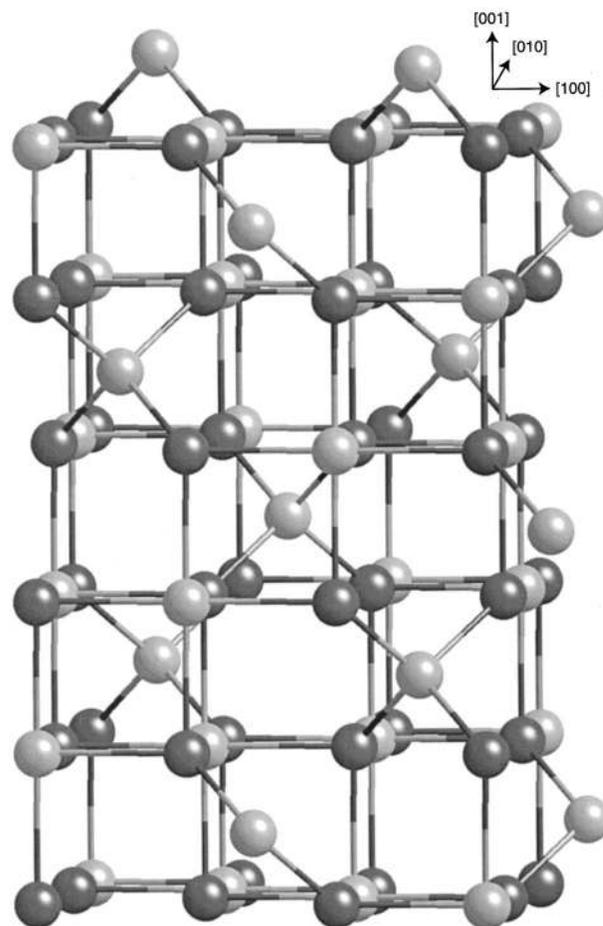


FIG. 3. Schematic representation of a 3/2 spinel unit cell (12 layers) of  $\gamma$  alumina with a low-density face uppermost.

## 2. Exposed low-density face

Figure 3 schematically shows a low-density layer exposed on the surface, for 3/2 of a spinel unit cell. The bulk-terminated low-density surface exposes tetrahedral aluminum atoms, which lack two out of four neighbors. We have considered several possible arrangements for the VSS; however we limit them to octahedral sites and no two VSSs are placed close together.

We first consider a six layer system (top half of Fig. 3) with three different distributions of two VSS: high-density layers (1,2), (1,3), and (2,3). We keep the bottom pair of layers frozen to their nominal bulk positions and allow the rest of the system to relax. The optimized structures of  $\gamma$  alumina, for the (1,2) and (2,3) choices of VSS, respectively, are shown in Fig. 4. Here, we take a different view angle, along the (110) direction, to better show the reconstruction.

In both cases, there is substantial reconstruction, involving the uppermost T atoms (compare to Fig. 3) falling into nonspinel sites in the bulk, along with other atoms moving to new sites. In Fig. 4(a), the spinel framework remains largely intact. In Fig. 4(b), however, there is clearly a massive reconstruction involving the formation of an entirely regular structure, with no vacant sites, and with a different symmetry. This structure has channels running along the (110) direction, formed by a reordering of the oxygen and aluminum

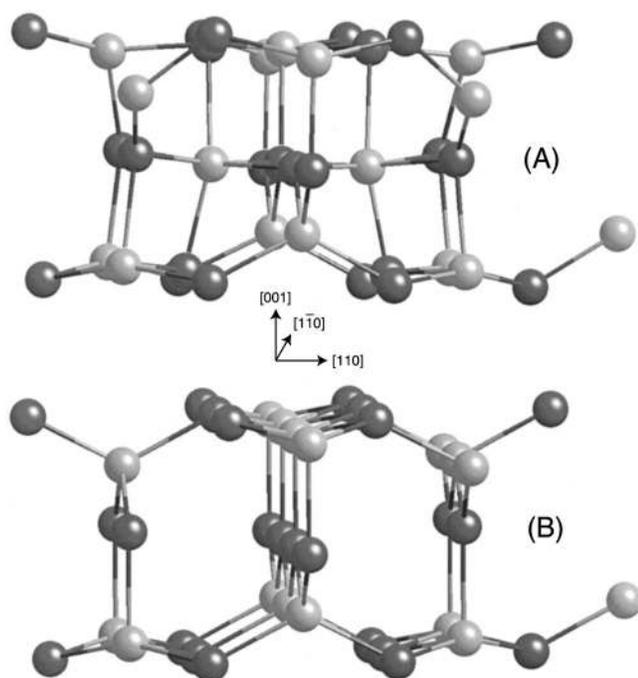


FIG. 4. Optimized six-layer structures of  $\gamma$  alumina when a low-density layer is exposed, with two choices of the VSS distribution. The view is along the (110) direction. Structure (b) has undergone a massive reconstruction, and is lower in energy than (a) by 4 eV.

atoms that originated in the middle high-density layer. This structure is of lower energy, by 4–5 eV, than the ones in which the spinel framework remains intact.

To test the validity of the surface reconstruction discussed above, we carried out three further sets calculations.

In the first set, we have allowed all layers in the six layer system to relax. In so doing, we no longer intend to simulate the uppermost layers of a bulk structure, but rather a thin film of  $\gamma$  alumina, such as may be relevant in catalytic systems. In these thin films, the overall structural features remain the same as those of the analogous surface calculations, albeit with some minor change in various atomic positions.

In the second set, we take the optimized structure that underwent a massive reconstruction [Fig. 4(b)] and augment it with another six spinel-like layers with three different choices of VSS distributions in the lower six layers. We then carry out energy minimizations, holding only the lowest two layers fixed, to see how far into the bulk the massive reconstruction may propagate. We call this a (6+6) arrangement.

Third, we take three twelve layer systems, with the same VSS distributions as in the (6+6) arrangements, but with all atoms beginning at their nominal spinel positions, and optimize the structure with the lowest two layers fixed. We call this a (12) arrangement. In additional calculations, we allow all layers to relax, simulating thereby a twelve layer thin film of  $\gamma$ -alumina.

In Fig. 5, we show the lowest energy optimized structure found among the (6+6) arrangements and the (12) arrangements, respectively. We can make several interesting observations.

In Fig. 5(a), the upper and lower set of six layers apparently behave independently, with the Al atoms in the low-

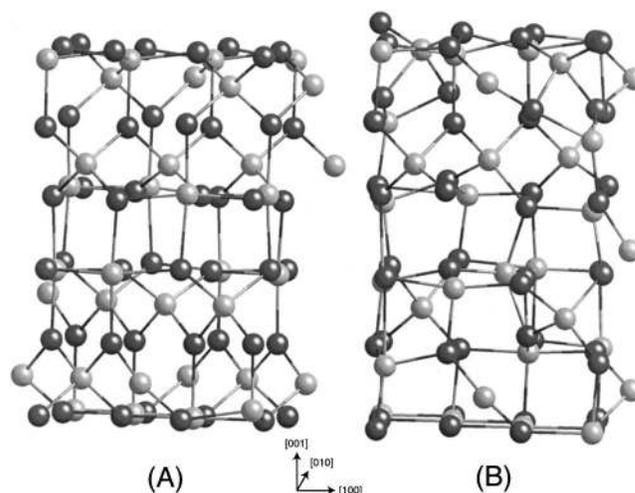


FIG. 5. (a) Optimized structure for a (6+6) arrangement, with the low-density layer exposed. (b) (12) arrangement whose VSS distribution corresponds to that in (a). Arrangement (a) is 10 eV lower in energy than (b).

density layer between them migrating downward, leaving the two sectors only weakly connected. In the case illustrated, the upper sector remains in its reconstructed form as in Fig. 4(b) (the reconstruction does not reverse upon adding six spinel layers below it), and the lower six layers undergo the same reconstruction as did the upper six, but with the channels oriented perpendicular to those in the upper sector. We have chosen an (010) view angle to emphasize that the two sectors are equivalent.

The reconstruction that occurs in the lower half of the (6+6) system does not mean that the original reconstruction has propagated downward, however. In the other VSS distributions we tried, no such reconstruction occurred, and so we rather consider the lower half to be largely independent of the upper half. This may be because the reconstruction in the upper half left it with few missing bonds below it, leaving little interaction between the two sectors. The case illustrated happens to be one in which the lower sector, independently of the upper, also preferred to reconstruct similarly, and is not an example of downward propagation of the original reconstruction.

On the other hand, when we optimize the twelve layer spinels with the same VSS distributions as the three (6+6) arrangements, none of the resulting structures resemble those obtained with the (6+6) assembly method. Figure 5(b) shows the lowest energy of the (12) arrangements, which also has the same initial VSS distribution as that of Fig. 5(a). In Fig. 5(b), however, all twelve layers remain much closer to the original spinel structure: although there is a great deal of distortion and cation migration, there is no concerted and symmetric rearrangement as in Fig. 5(a). The energy of each (6+6) arrangement is lower than its corresponding (12) arrangement, by 4.5–18 eV.

On comparing the (12) arrangement systems (with their lowest layers frozen) with the corresponding thin films (all layers movable), we find that letting the bottom pair also relax does not change the structural features appreciably. The energy decreases, as expected, because the frozen atoms are now able to relax away from their nominal spinel positions.

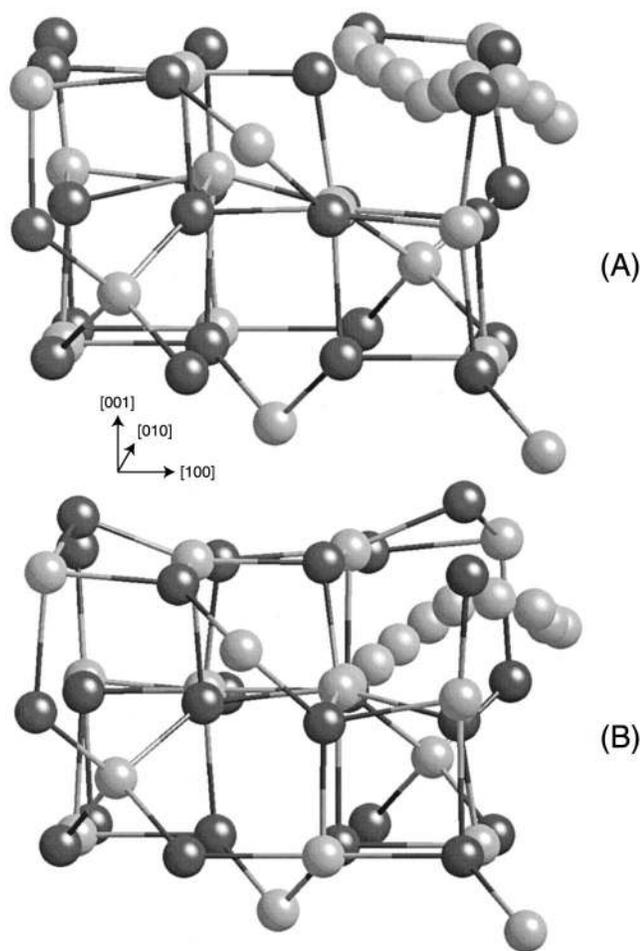


FIG. 6. (a) Minimum energy path for the hopping of an Al atom from a  $T$  spinel site near the surface to an O spinel site on the surface. The motions of surrounding atoms are not shown explicitly. (b) Same as (a), for an Al atom hopping from a  $T$  spinel site near the surface to an O spinel site in the bulk region.

We find that this relaxation energy is 2–6 eV. Since the bottom layers have the high-density surface exposed, we do not expect as much relaxation, but some unfavorable VSS distributions apparently allow for a comparatively greater reconstruction, and energy decrease, to occur upon being considered a thin film rather than a bulk.

These observations indicate that the detailed structural features of a  $\gamma$ -alumina surface depend upon the mode of preparation: that is, a thin layer may have a very different structure than a thicker layer, thus affecting the catalytic properties of  $\gamma$  alumina. We note that a massive surface reconstruction has also been found in  $\gamma$  alumina when the (110C) face is exposed.<sup>24</sup>

### C. Kinetics of the VSS distribution: VSS migration

The above observations on the energetics of various configurations of VSS in  $\gamma$  alumina now pose the question of vacancy migration from the surface to the bulk. We have studied the vacancy migration process in a low energy six layer system with a high-density surface exposed.

We have calculated the minimum energy path for this process (which of course is actually the migration of an Al

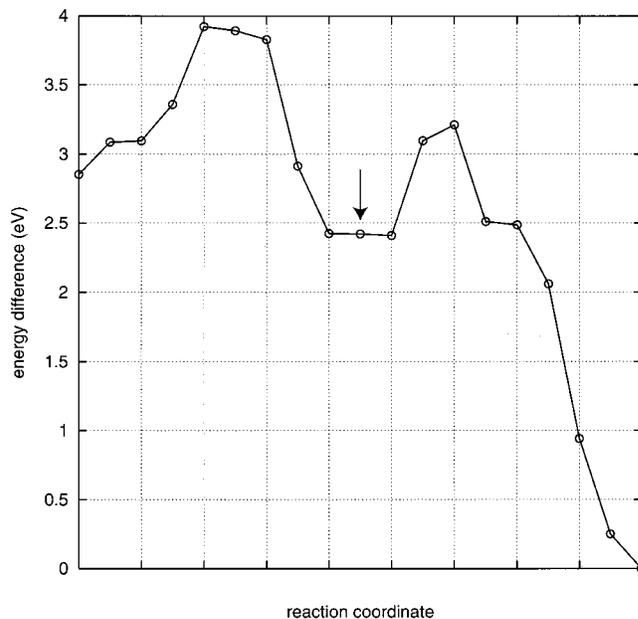


FIG. 7. Energy barrier for VSS migration in  $\gamma$  alumina corresponding to those shown in Fig. 6. The arrow refers to the situation when there is a vacant  $T$  spinel site near the surface. Left of the arrow is shown the potential energy for the vacant spinel site to move to an O spinel site on the surface, and right of the arrow is the energy for the vacant  $T$  site to move to an O spinel site in the bulk region.

atom in the reverse direction) using the nudged elastic band (NEB) method.<sup>55</sup> Figure 6 shows the calculated atomic positions for the moving aluminum atom for the two steps in the overall vacancy migration. The other atoms, particularly a few nearby oxygens, also are slightly involved in the minimum energy path, but their motion is omitted for clarity. The energy along the path is shown in Fig. 7.

In the first step [Fig. 6(a)] we start from (T5,O2) and go to (O12,O2). This amounts to the migration of an aluminum atom from an O spinel site on the surface to a nearby vacant  $T$  spinel position, thereby creating a VSS on the surface. In the second step [Fig. 6(b)] we start from the (O2,O8) arrangement and go to (T5,O2). In this case, the vacancy does not lie on the surface and an aluminum atom moves from a  $T$  site near the surface to a nearby O site in the bulk region, thus creating a VSS on a  $T$  site near the surface. Together these paths describe the migration of a VSS from an O site in the bulk region to an O site on the surface, via a  $T$  site in the intervening layer, (O12,O2)  $\rightarrow$  (T5,O2)  $\rightarrow$  (O8,O2).

The energy barriers for VSS migration (see Fig. 7) are 1 eV to go from surface to bulk and 3 eV in the reverse direction. Since these barriers are so high, the distribution of VSS, as created in the process of the preparation of  $\gamma$  alumina, will be frozen in at room temperature. This finding is consistent with a NMR study of  $\gamma$  alumina by Lee *et al.*<sup>13</sup> in which they found that the NMR peak shape and position remained unchanged on going from 120 to 293 K. Lee *et al.* also concluded that the disorder in the positions of Al in  $\gamma$  alumina, that is the distribution of O and  $T$  VSS, becomes fixed already at a high temperature, and no subsequent ordering takes place.

#### IV. SUMMARY

In the present study, we studied the (001) surface of  $\gamma$  alumina and we found several important features relating to the vacant spinel site (VSS) distribution and the surface structure. First, octahedrally situated VSS are preferred by 2–3 eV over tetrahedral sites. Second, any configuration involving many nearby missing bonds is unfavorable: this encompasses a repulsion between neighboring VSS (because then some oxygen atoms are missing two aluminum neighbors). Third, the VSS are repelled from the surface, presumably because Al atoms that occupy the surface can benefit more than bulk Al atoms from surface relaxation, which is large in this system. Fourth, with the low-density bulk-terminated surface exposed, we find that a reconstruction occurs which at least involves the descent of the uppermost tetrahedral Al atoms into the bulk, together with further rearrangement, and in some cases the spinel structure may actually collapse into a very different, nondefective structure. This massive reconstruction only occurs for thin layers of  $\gamma$  alumina, however, and suggests that the structure of catalytic  $\gamma$ -alumina systems may be quite different from the normal spinel. We have also found that the energy barrier for vacancy migration is very large. This is consistent with an earlier study of a bulk  $\gamma$ -alumina system,<sup>1</sup> which found that the vacancy distribution is frozen in already well above room temperature.

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