

## Theoretical structure determination of $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

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(Received 27 June 2001; published 29 November 2001)

$\gamma$ -alumina is usually described as a defect spinel structure with cation site vacancies distributed randomly between octahedral and tetrahedral positions. Its structure and properties are still not well understood. Using *ab initio* calculations based on density functional theory and plane-wave pseudopotentials, we investigate all possible vacancy configurations within a 40-atom unit cell, which are consistent with the crystallographic data available. We find that the minimum energy structure has all the vacancies located at octahedral sites. Results are presented for the atomic configuration, bulk modulus, and electronic density of states of this structure.

DOI: 10.1103/PhysRevB.65.012101

PACS number(s): 61.50.Ah, 61.66.-f, 61.72.Bb, 71.20.-b

Aluminum oxide, Al<sub>2</sub>O<sub>3</sub>, traditionally referred to as alumina, is a very important ceramic material which has many technological applications. Its great usefulness as a material rests primarily on its extreme hardness (Moh 9), high melting point (2327 K), and low electrical conductivity (10<sup>-12</sup> S/m at 20 °C). It has a wide range of application, from electronics, optics, biomedical, and mechanical engineering to catalyst support.

Among the many polymorphs of alumina, the thermodynamically stable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, or corundum, has been studied most extensively, both experimentally and theoretically. However, there are many metastable structures, the so-called “transition aluminas,” which so far are not well understood (see, for example, Ref. 1, and for a more recent review see Ref. 2). One of them is  $\gamma$ -alumina. Due to its unique properties like high surface area and mechanical strength, it has been used as catalyst and catalyst support. Its use is based only on empirical considerations, and it would be very useful to know its atomic and electronic structure.

Since the pioneering work of Verwey in 1935,<sup>3</sup> the structure of  $\gamma$ -alumina is usually described as a defective spinel, denoted as  $\square_2 \frac{2}{3} \text{Al}_{21 \frac{1}{3}} \text{O}_{32}$ , ( $\square$  = vacancy). This formula is deduced from the fact that a spinel cubic cell (typified by MgAl<sub>2</sub>O<sub>4</sub>) has 32 O atoms on a fcc lattice and 24 cation sites in tetrahedral and octahedral positions. In order to satisfy the Al<sub>2</sub>O<sub>3</sub> stoichiometry, one must introduce an average of  $2\frac{2}{3}$  cation vacancies per cell.<sup>4</sup> An integer number of Al atoms is obtained if one enlarges this unit cell by a factor of 3, to have a cell containing 160 atoms, with 96 O atoms, 64 Al atoms, and 8 cation vacancies. There has been a long-standing debate as to whether these vacancies occupy octahedral or tetrahedral cation sites, and in what proportions. So far, there is no agreement about this point, although there is a broad consensus that they do not form an ordered sublattice but appear to be randomly placed throughout the unit cell.

Experimental results, including neutron, electron, and x-ray diffraction, have led to conflicting conclusions that the vacancies are situated entirely in octahedral positions,<sup>3,5,6</sup> entirely in tetrahedral positions,<sup>7-9</sup> or as in the case of recent NMR measurements,<sup>10</sup> in both sites, with an approximative

proportion of 63:37 for the tetrahedral and the octahedral sites, respectively. Theoretical studies have not led to a conclusive result either. An early molecular-dynamics (MD) simulation by Alvarez *et al.*<sup>11</sup> showed that 64% of the vacancies prefers tetrahedral sites. This result is supported by the theoretical work done in Ref. 10, which combines *ab initio* energy calculation with a Monte Carlo simulation. However, Mo *et al.*,<sup>12</sup> based on an empirical pair potential calculation and first-principles structure studies, have concluded that cation vacancies are preferentially located at the octahedral sites. The same conclusion was obtained by Streitz and Mintmire<sup>13</sup> in a very recent MD simulation using an empirical potential (which explicitly includes a variable charge transfer between anions and cations), although these authors also note that the energy cost for a modest occupation of tetrahedral sites is small.

In this contribution we report on first-principles total energy calculations based on density functional theory (DFT),<sup>14,15</sup> which have been demonstrated to be a powerful and effective method to tackle structural problems.<sup>16</sup> Our main goal is to resolve the uncertainties regarding the atomic structure of  $\gamma$ -alumina as well as present results of its electronic structure, opening the way to further investigations in this material.

In the search for the minimum energy structure, the total energies for a large number of configurations consistent with the crystallographic specifications need to be calculated. For  $\gamma$ -alumina, the fractional number of Al atoms represents an additional difficulty. At this point two main alternative, approximate ways have been put forward. In most MD simulations the authors have increased the unit cell, in order to have an integer number of Al atoms, and have chosen at random a number of different configurations, in the hope that they are representative.<sup>17</sup> Another way is that of Ref. 12, where a cubic cell was adopted with 32 O atoms, 21 Al atoms, and 3 vacancies as a tolerable approximation to the stoichiometric  $\square_2 \frac{2}{3} \text{Al}_{21 \frac{1}{3}} \text{O}_{32}$ . In this work we follow a different and more accurate approach. According to the hint given by Sohlberg *et al.*,<sup>18</sup> instead of considering the cubic cell, one can consider a primitive cell with fewer particles. This allows us to have a cell containing 24 O atoms, 16 Al,

and two cation vacancies, with only 153 configurations. In the following, we describe the construction of the cell, the method of calculation, and finally we discuss the results.

The cell that we investigate was constructed in the following way. We begin with an ideal spinel unit, typified by  $\text{MgAl}_2\text{O}_4$ , with the lattice constant corresponding to that of  $\gamma$ -alumina,  $a = 7.911 \text{ \AA}$ . This fcc cubic cell has 56 atoms, 8 Mg atoms in tetrahedral positions, 16 Al in octahedral positions, and 32 O in a fcc array. Then we replace the Mg atoms by Al atoms, getting  $\text{Al}_{24}\text{O}_{32}$ . The key point is to note that the primitive cell has 14 atoms, with the formula  $\text{Al}_6\text{O}_8$ . We stack then three of these primitive cells on “top” of each other, obtaining a cell with 18 Al and 24 O atoms. To get the correct stoichiometry, we need to remove two Al atoms. In this way we obtain a cell with 40 atoms, containing 8  $\text{Al}_2\text{O}_3$  formula units. The two vacancies can be located both in octahedral positions (referred to as OO from now on), one in an octahedral position and the other in a tetrahedral position (OT), or both in tetrahedral positions (TT). The total number of such combinations is 153 (66 are OO, 72 OT, and 15 TO). Analyzing these configurations we found that there are only 14 inequivalent configurations from which 4 are OO, 6 TO, and 4 TT.

We performed total-energy calculations for all these 14 configurations, allowing for relaxations, in the framework of DFT within the local-density approximation (LDA), using the exchange-correlation functional of Ceperley and Alder.<sup>19</sup> All calculation were done using the *ab initio* total-energy and molecular-dynamics program VASP (Vienna *ab initio* simulation program) developed at the Institut für Theoretische Physik of the Technische Universität Wien.<sup>20–22</sup> The ions are represented by ultrasoft Vanderbilt pseudopotentials<sup>23</sup> and the valence orbitals are expanded in a basis including plane waves up to a kinetic energy cutoff  $E_{cut}$ . Observe that the LDA is sufficient to support our results, not being necessary to use the generalized gradient approximation (GGA) at this level. In fact, in a very recent work<sup>24</sup> were performed extensive comparisons between the LDA and GGA for alumina, concluding that for structural properties and geometry optimization there is not a “clear winner in terms of physical accuracy between LDA and GGA in describing  $\text{Al}_2\text{O}_3$ .”

Preliminary test calculations were performed for three different vacancy configurations using  $E_{cut}$  ranging from 300 to 700 eV and  $\mathbf{k}$ -point samplings including the  $\Gamma$  point and  $(1 \times 1 \times 3)$ ,  $(2 \times 2 \times 6)$ ,  $(3 \times 3 \times 9)$ , and  $(5 \times 5 \times 15)$   $\mathbf{k}$ -point meshes. These tests show that the convergence in  $E_{cut}$  is much faster than the convergence in  $\mathbf{k}$ -point sampling. An  $E_{cut}$  of 400 eV turned out to be sufficient and this is the value we used in all our further calculations. Regarding the  $\mathbf{k}$ -point sampling, the energy differences for the test cases were converged to  $0.03 \text{ eV}/(\text{Al}_2\text{O}_3)$  when using only the  $\Gamma$  point and to  $0.004 \text{ eV}/(\text{Al}_2\text{O}_3)$  when using a  $(3 \times 3 \times 9)$   $\mathbf{k}$ -point sampling (19  $\mathbf{k}$  points in the irreducible wedge of the Brillouin zone). Based on this test, we performed low- and high-accuracy calculations depending on the stage of the calculations. In order to obtain the total energy for all 14 initial unrelaxed configurations and for the first part of the relaxation procedure, we performed low-accuracy calculations, using only the  $\Gamma$  point. After that, we performed high-

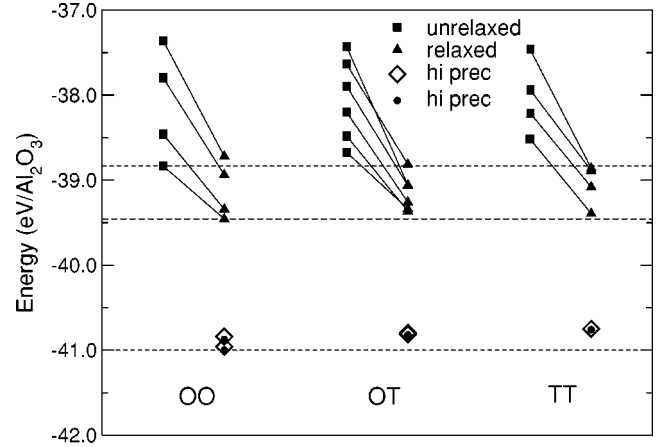


FIG. 1. Total energy of the 14 different configurations, before and after relaxation. OO, OT, and TT denote configurations with two octahedral vacancies, one tetrahedral and one octahedral vacancy, and two tetrahedral vacancies, respectively. Square (triangles) denote unrelaxed (relaxed) low-accuracy calculation, whereas diamond (circles) denote high-accuracy relaxation without (with) volume relaxation. Note that the two lowest OT structures are practically indistinguishable on this scale

accuracy calculations for all our final results involving the five lowest-energy structures, using a  $(3 \times 3 \times 9)$   $\mathbf{k}$ -point mesh.

In Fig. 1 we display the results of total-energy calculations for all 14 inequivalent configurations. The initial, unrelaxed configurations corresponding to OO, OT, and TT configurations are shown by black squares. We can see that the minimum energy configuration corresponds to an OO structure, followed by an OT, and then a TT configuration, with energy differences of  $0.160 \text{ eV}/(\text{Al}_2\text{O}_3)$  and  $0.317 \text{ eV}/(\text{Al}_2\text{O}_3)$ , respectively. The triangles show the energy of

TABLE I. Calculated crystallographic data for  $\gamma$ - $\text{Al}_2\text{O}_3$ .

Ideal spinel, $\text{Al}_2\text{O}_4$ , space group $Fd\bar{3}m$ , origin at $-3m$				
Atom	Wyckoff notation	x	y	z
Al(tet)	8(a)	0.5	0.5	0.5
Al(oct)	16(d)	0.125	0.125	0.125
O	32(e)	0.255	0.255	0.255
Basis vectors	(0,1/2,1/2)			
	(1/2,0,1/2)			
	(3/2,3/2,0)			
Vacancy positions:	(1/2,1/2,1/6)			
	(1/2,1/2,2/3)			
Lattice constant	$a = 7.911$ (experimental)			
	$a = 7.887$ (calculated)			
Calculated bulk modulus	$B = 219 \text{ GPa}$			
Bond lengths ( $\text{\AA}$ )				
Al(tet)-O	1.78			
Al(oct)-O	1.94			
O-O	2.70			

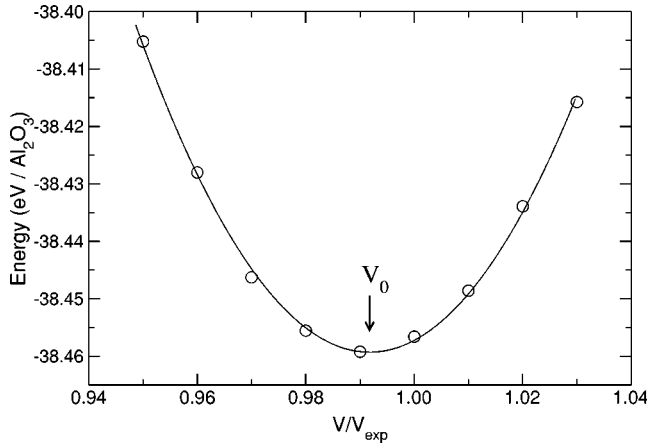


FIG. 2. Calculated total-energy curve as a function of the crystal volume.  $V_0$  corresponds to the calculated volume and  $V_{exp}$  is the experimental volume.

these configurations after relaxation.

It should be noted that relaxation has a significant effect on the relative ordering of the structures. Within each of the groups OO, OT, and TT, the energy difference between the highest and lowest configurations decreases after relaxation. For example, the highest-energy TT structure relaxes to become very close in energy to the structure below it. The relaxation effects are strongest for the OT structures. The highest-energy structure relaxes very strongly and the lowest two configurations change order after relaxation. The relative ordering between the groups is also changed. The lowest-energy configuration is still an OO structure, but now followed by a TT and then an OT configuration. The difference in energy between these lowest-energy structures is even smaller than in the unrelaxed case, close to the accuracy limit of this calculation.

In order to obtain more precise results, we performed higher-accuracy calculations using 19  $k$  points, to relax the

five lowest-energy configurations: two OO, two OT, and one TT structure. The results are shown in Fig. 1, where the diamonds denote the internally relaxed structures without volume relaxation and the circles denote fully relaxed structures, i.e., positions and volume. We can see that the relative ordering of the structures has changed again: the lowest-energy configurations are now the two OO structures [at  $-40.998$  and  $-40.874$  eV/( $\text{Al}_2\text{O}_3$ )], followed by the two OT, which are very close in energy [ $-40.836$  and  $-40.821$  eV/( $\text{Al}_2\text{O}_3$ )], and finally the TT configuration [ $-40.760$  eV/( $\text{Al}_2\text{O}_3$ )].

From our results it can be safely concluded that the minimum energy structure of  $\gamma$ -alumina does not correspond to a structure containing only tetrahedral Al vacancies. Moreover, although the OO and OT arrangements are close in energy, within the accuracy of our calculation it follows that the minimum energy structure of  $\gamma$ -alumina corresponds to a structure containing *only octahedral* Al vacancies. In Table I we present the crystallographic properties for this structure, like the inequivalent positions of the ideal  $\text{Al}_2\text{O}_4$  spinel structure, the starting point for constructing our structure. Then the choice of our basis vectors is shown and the positions of the two octahedral vacancies relative to this basis. The salient feature with respect to the other OO configurations is that it is the one where the distance between the Al vacancies is the largest. For this configuration we calculate the total-energy versus volume curve, shown in Fig. 2. The calculated volume is close to the experimental volume and underestimates it by only 1%. Performing a quadratic fitting to this curve we estimate the bulk modulus for  $\gamma$ -alumina to be  $B = 219$  GPa, the lowest one of the known values for the alumina polymorphs.

In Fig. 3 we show the electron density of states (DOS) for the OO, OT, and TT minimum energy configurations, together with the x-ray photoelectron (XPS) measurements done by Ealet *et al.*<sup>6</sup> The calculated density of states of the three configurations presents similar features, as in the case

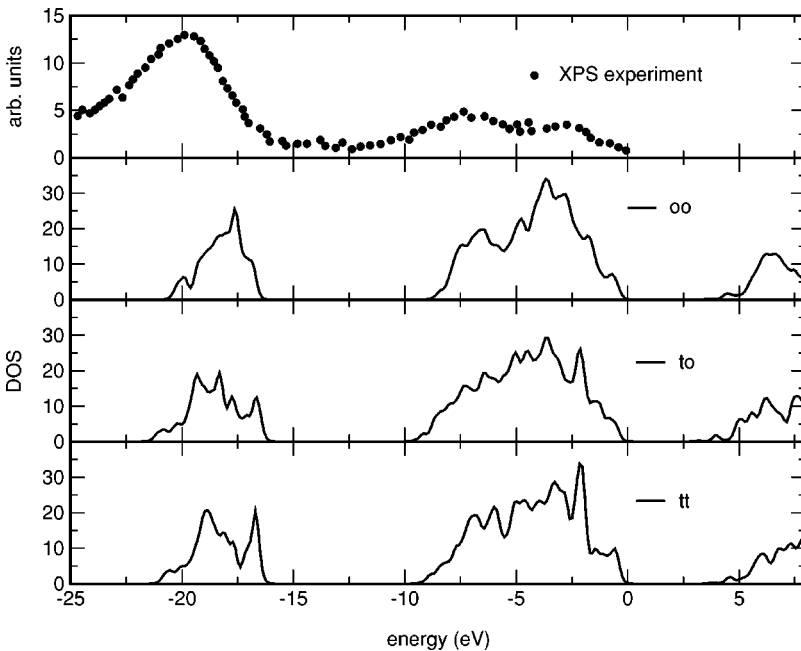


FIG. 3. Experimental XPS data and calculated density of states for the configurations with the two vacancies occupying octahedral (OO), one octahedral and one tetrahedral (OT), and both tetrahedral (TT) positions, respectively. The top of the valence band is set to 0 eV.

of  $\alpha$ - and  $\kappa$ -alumina, all reflecting the Al-O bonding.<sup>25</sup> The electronic states of the upper valence band (UVB) are dominated by O  $2p$  states. The corresponding width is about 9 eV, while the experimental value is 9.5 eV. The UVB is separated by a gap of about 7 eV from the lower valence band (LVB), composed of O  $2s$  states, with a width of about 5 eV. The band gap between the UVB and the conduction band obtained in our calculation is rather small, 4.0 eV, compared with the 8.7 eV reported from an energy loss spectrum experiment.<sup>6</sup> In order to check this value, we calculated the band gap of  $\alpha$ -alumina (which is 8.7 eV according to experiments<sup>26</sup>) using the same method and obtained a value of 6.3 eV. This value compares well with the values reported in the literature, which range between 6.2 and 6.6 eV, depending on the method used. This type of underestimation of the energy gap is a well-known problem of DFT.<sup>15</sup>

Examining in more detail the total DOS corresponding to the three configurations, one can see that some important differences exist, especially between the OO and TT configurations, which are also the most different from each other in structure. The LVB of the OO configuration shows only one main peak, while in the case of TT we can see two peaks. On the other hand, the UVB of the OO has two peaks, but the UVB of TT shows a broad distribution, without any distinguishable peaks. If one compares the DOS of these two configurations with the experimental XPS result, it is clear that it is the OO DOS which resembles the most the experiment. The two maxima below the Fermi energy in the XPS curve, at  $-3.16$  and  $-5.47$  eV, correspond to the ones at about  $-3$  and  $-6.5$  eV in the UVB of the OO DOS. In the same

way, one can relate the broad peak in the XPS curve at  $-20.3$  eV with the peak at  $-17.5$  eV in the LVB of the OO DOS.<sup>27</sup> It is interesting to note that in our case the differences between the OO and TT DOS are more clear than in the case of the results obtained by Mo *et al.*,<sup>12</sup> as well as that our agreement with the XPS data is better. The overall picture of the DOS gives additional support to the conclusion that cation vacancies prefer octahedral sites.

In summary, we have performed accurate first-principles calculations to determine the crystallographic structure of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. According to our results, the cation vacancies are located on octahedral sites, at positions that are most far away from each other. However, there are two points which deserve more attention. First, we have used a rather limited supercell in our calculations, and further work is needed to check the degree of dependence of the results on this. Second, the gain in energy compared to structures with Al vacancies located at tetrahedral sites is modest, and it is likely that at finite temperature the structure will also have some Al vacancies located on tetrahedral sites. We hope the present work will provide useful information that will help to resolve the outstanding uncertainties regarding the interpretation of the experimental data and encourage new theoretical work for this important material.

We would like to acknowledge Pavel Korzhavyi for interesting discussions. G.G. was supported by the Faculty of Science and Technology, Uppsala University, FONDECYT (Chile), under Grant No. 1010126, and by *Iniciativa Científica Milenio*, ICM P99-135-F (Chile). Part of the calculations were performed on the CRAY T3E of the National Supercomputer Center in Linköping, Sweden.

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