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ARTICLES

Theoretical investigation of the structure of κ -Al₂O₃

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Using plane-wave pseudopotential calculations based on density-functional theory at the local-density-approximation level we investigate all the possible κ -Al₂O₃ structures which are permitted by the known crystal symmetry. We find that structures with sixfold coordinated Al atoms are significantly more stable than those having any or all of the Al atoms in fourfold coordinated sites. This is in agreement with preliminary experimental results. [S0163-1829(97)01914-0]

I. INTRODUCTION

Metal oxides such as Al₂O₃ (alumina) are important in many technical applications. An increasing number of these applications demand a more fundamental understanding of the properties of these materials. To indicate the wide range of uses that have been found for alumina, we mention that the stable and well-characterized α -Al₂O₃ phase is used in applications ranging from structural ones in cutting-tool manufacturing, optical ones in laser manufacturing, to electronic ones as a substrate for epitaxial growth of Si in electronic-device fabrication. In this paper we study the structure of κ -Al₂O₃, which is one of the many different phases of alumina. Other phases include the above-mentioned stable α phase and the metastable β , γ , η , κ , θ , and χ phases.

In the present work our main interest is in structural properties. An improved understanding of the κ phase is of particular interest in this context since both the κ and the α phases are used as wear-resistant coatings on cemented carbides in cutting-tool materials. In these applications the κ phase has advantages over the α phase due to its smaller grain size, lower density of pores, and more well-behaved epitaxial growth. These advantages must, however, be weighted against the disadvantage of the metastability of the κ phase, which undergoes a phase transition to the α phase at about 1200 K. It would be desirable to understand the atomic-scale mechanism of this phase transition. Unfortunately, this is not possible since the microstructure of the κ phase is not known.

As far as earlier work is concerned, the fact that the atomic structure of α -Al₂O₃ has been accurately known for a long time has resulted in a large number of both theoretical and experimental studies of this phase.¹⁻⁸ These studies include both confirmations of the microstructure and determination of other properties starting from the known atomic positions in the unit cell.

For κ -Al₂O₃ only a few experimental studies are available.⁹⁻¹² Both theoretical and experimental work has so far most certainly been hampered by the lack of knowledge

about the atomic positions within the unit cell which is often a prerequisite for further studies. The aim of this paper is to partly resolve this difficulty by substantially reducing the number of possible structure models.

The paper is organized as follows. In Sec. II we describe the crystal-structure models that can be deduced from experimental work. In Sec. III our method of calculation is outlined. In Sec. IV we present our results. Finally, in Sec. V we summarize our findings.

II. STRUCTURE

Using convergent-beam electron diffraction⁹ and transmission-electron microscopy (TEM), Skogsmo *et al.*^{9,10} have found that the crystal structure of κ -Al₂O₃ belongs to the orthorhombic crystal system with the point group $mm2$ and the space group $Pna2_1$. A recent study¹¹ using x-ray diffraction (XRD) has confirmed this suggestion. There is now agreement that the earlier suggestion of a hexagonal structure¹³ must be replaced by one where a superlattice composed of three orthorhombic twin-related cells are rotated relative to each other by 120°.^{9,10}

In an atomic model for κ -Al₂O₃ based on these experimental results, the orthorhombic unit cell has four O layers and four Al layers. The oxygen planes are in a close-packed *ABAC* stacking sequence along the *c* axis, with in-between aluminum planes as shown in Fig. 1(a), and the Al ions are allowed to have octahedral and/or tetrahedral positions, as shown in Fig. 1(b). The unit cell contains eight molecular units, i.e., 40 atoms, 16 Al, and 24 O. The room-temperature lattice parameters have been reported¹¹ to be $a=4.8351$ Å, $b=8.3109$ Å, $c=8.9363$ Å. As XRD can be expected to provide more accurate numbers in this context, we choose to use these parameters rather than those of Ref. 9.

The uncertainty regarding the κ -Al₂O₃ structure is entirely related to the atomic positions within the aluminum layers which we now study more closely. Each Al layer consists of four Al atoms to be distributed on 18 positions. However, each of these positions has one symmetry related posi-

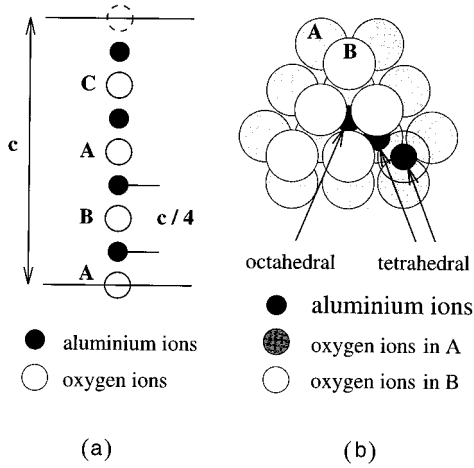


FIG. 1. (a) Structure layering: the structure projected onto the c axis schematically shows the alternating Al and O layers. (b) Al positions in a plane: three different Al positions between two oxygen layers with stacking A and B are shown, two in tetrahedral positions and one in an octahedral position.

tion in the same layer, pairing the possible positions. This leads to a total of 36 different ways to arrange the Al atoms in a layer. This number can be reduced by noting that it is energetically unreasonable to have Al atoms in immediately adjacent octahedral and tetrahedral sites. This brings the number of possible layers down to 13. Of these 13 layers, 3 have all Al atoms in octahedral positions (O layers), 6 layers have all Al atoms in tetrahedral positions (T layers), and 4 layers have Al atoms in both octahedral and tetrahedral positions, we denote these layers mixed (M layers). We will further refer to structures with no M layers as “unmixed.”

To determine the possible structure models for the whole κ - Al_2O_3 unit cell we must consider the fact that due to the 2_1 symmetry axis defined by the space group $Pna2_1$, the Al layers n and $n+2$ are related. Of the four aluminum layers there are consequently only two layers which can be regarded as independent. With 13 possibilities for each layer, there are thus $13^2=169$ possible structure models for κ - Al_2O_3 . We will present results for all of these models.

The analysis of the symmetry-permitted structures can be pushed a bit further if we make the additional assumption

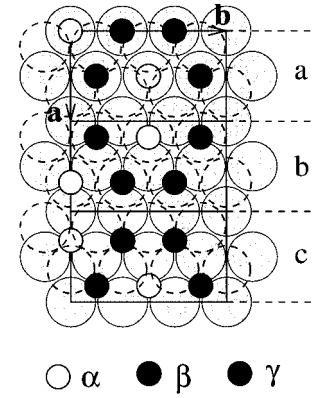


FIG. 2. Vacancy positions: the α , β , and γ vacancy positions for Al layers in the a , b , and c positions are shown [the oxygen layers are in the A position (solid circle) and B position (dashed circle)].

that no M layers are present. Since experimental results are often analyzed with this assumption,¹² we introduce below the concepts which this leads to. For future reference we note that using only unmixed layers we have $(3+6)^2=81$ possible unmixed structures.

Using now only layers where all Al atoms have the same coordination, it becomes natural to divide the description of the Al positions into the stacking sequence of the Al layers, and the position of the vacancies which are inevitably present since there are not enough Al atoms available to fill the Al layers.

We first look at the stacking sequence of the Al layers. This is characterized by a , b , and c (relative to the oxygen A layer, cf. Fig. 2). Due to the earlier mentioned 2_1 symmetry axis, layers n and $n+2$ are related in such a way that if n is a , b , or c , then the layer $n+2$ is a , c , and b , respectively. With two independent layers and three possible stackings of each layer there are a total of nine stacking sequences for the unmixed structures.

The next issue concerns the positions of the vacancies. Within the unit cell each unmixed Al layer consists of four Al atoms and two vacancies for a total of six atomic positions. However, as with the Al atoms described in the general case considered earlier, the vacancy positions are paired

TABLE I. Convergence test for the energy difference in eV/atom between two structures (I and VIII, see Table III), with respect to both the plane-wave energy cutoff and the k -point sampling. N_{BZ} is the total number of k points in the Brillouin zone; N_{used} is the number of k points actually used in the computations after symmetry considerations.

k set	k -point sampling	No. of k points		Plane-wave cutoff			
	k -point positions	N_{BZ}	N_{used}	550 eV	600 eV	650 eV	700 eV
I.1	(0 0 0)	1	Γ	-0.345	-0.351	-0.353	-0.354
I.2	$(\pm \frac{1}{4} 0 0)$	2	1	-0.343	-0.347	-0.350	-0.351
I.3	$(\pm \frac{1}{4} \pm \frac{1}{4} \pm \frac{1}{4})$	8	4	-0.340	-0.346	-0.347	-0.348
I.4	$[(\pm \frac{1}{8} \pm \frac{1}{4} \pm \frac{1}{4}), (\pm \frac{3}{8} \pm \frac{1}{4} \pm \frac{1}{4})]$	16	8	-0.342	-0.346	-0.349	-0.350
I.5	$[(\pm \frac{1}{8} \pm \frac{1}{8} \pm \frac{1}{8}), (\pm \frac{1}{8} \pm \frac{1}{8} \pm \frac{3}{8})]$ $[(\pm \frac{1}{8} \pm \frac{3}{8} \pm \frac{1}{8}), (\pm \frac{1}{8} \pm \frac{3}{8} \pm \frac{3}{8})]$	64	16	-0.341	-0.346	-0.347	-0.348

TABLE II. Comparison of total energies of κ -Al₂O₃ structures in different groups for both LDA and post-LDA GGA. The presented energies are the minimum energy in each group. A cutoff energy of 650 eV and 8 k points are used. ΔE is the energy difference relative to the group with the lowest energy.

Group	Stacking layer	LDA		GGA	
		E_{tot} (eV/atom)	ΔE (eV/atom)	E_{tot} (eV/atom)	ΔE (eV/atom)
1	OOOO	-284.374	0.000	-285.924	0.000
2	OMOM	-283.138	1.236	-284.580	1.344
3	MOMO	-283.093	1.281	-284.541	1.383
4	MMMM	-282.435	1.939	-283.980	1.944
5	TOTO	-282.175	2.199	-283.728	2.196
6	OTOT	-281.894	2.480	-283.359	2.565
7	MTMT	-280.631	3.743	-282.130	3.794
8	TMTM	-280.485	3.889	-282.028	3.896
9	TTTT	-279.450	4.924	-280.875	5.049

by symmetry. These vacancy pairs are labeled α , β , and γ , as illustrated in Fig. 2. Analogously with the layer stacking, the vacancy positions in Al layers 3 and 4 are determined by the positions in Al layers 1 and 2. With three possible vacancy positions in each of these two layers there are a total of nine possible vacancy configurations in an unmixed unit cell. Since each of these vacancy configurations can be combined with an arbitrary stacking sequence there is a grand total of $9 \times 9 = 81$ possible unmixed structure models for κ -Al₂O₃.

As mentioned previously, an analysis of experimental XRD data has been carried out by Halvarsson *et al.*¹² for different structure models of κ -Al₂O₃. By considering the space-group symmetry, orientation relationships, and density measurements of the possible structure models, they have suggested $Ac^\gamma Bc^\beta Ab^\beta Cb^\gamma$ as the most probable structure model. Note that in this structure all Al atoms are in octahedral positions and the vacancies are ordered along lines.

We would like to point out that many of the structures we investigate in this study may well be unstable. This is why we limit ourselves to unrelaxed, experimental, coordinates. We thus use our calculations as a sort of computer experiment which enables us to rule out most of the structures, thereby setting the stage for a more careful investigation of the remaining possibilities.

III. METHOD OF CALCULATION

Our calculations are based on the density-functional theory^{14,15} at the local-density-approximation¹⁶ (LDA) level and pseudopotentials. The pseudopotentials used for oxygen and aluminum are the norm-conserving potentials of Troullier and Martins¹⁷ ($r_c = 1.45$ bohr) and Bachelet *et al.*,¹⁸ respectively.

We employ a supercell approach and expand the one-electron wave functions in a plane-wave basis with a cutoff energy of 550–650 eV. The Kohn-Sham (KS) equations are solved iteratively with ever improving guesses for the self-consistent electronic ground-state density. In each iteration the KS Hamiltonian is diagonalized in the (orthonormalized) subspace of the trial one-electron wave functions and the total-energy gradients with respect to these. The output electronic density is calculated from the orbitals with the lowest expectation values and then the input electron density for the

next iteration is constructed by means of a Pulay mixing scheme that tries to guess an accurate input density using information about input and output densities in the previous iterations. The used method, which we call the damped density method¹⁹ (DDM), is quite similar to the method which Kresse and Furthmüller²⁰ call the residual minimization method. The methods only differ slightly in the algorithm used to diagonalize the KS Hamiltonian.

Our total-energy pseudopotential implementation has been used previously to successfully describe, e.g., the tiny energy differences of stacking faults in aluminum,²¹ and we have verified the new DDM scheme by repeating some of the calculations presented in this paper with the original code which uses the alternating conjugate-gradient minimization²² and subspace rotation method.²³

To reduce the number of k points needed, we use a finite electronic temperature of 0.1 eV when determining occupation numbers, and then extrapolate all total energies to zero electronic temperature.^{23,24} To ensure that our calculations are sufficiently converged with respect to the number of k points and the plane-wave energy cutoff, we have tested several combinations of Monkhorst-Pack²⁵ k -point samplings and plane-wave cutoffs, as listed in Table I. From these tests we conclude that (1) the energy differences are converged within 0.002 eV/atom using eight k points and a 650 eV

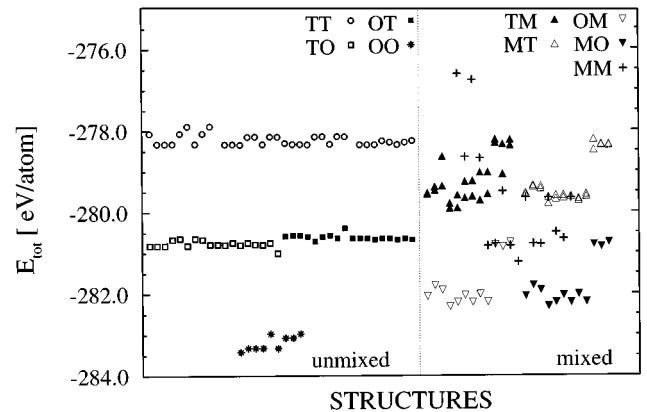


FIG. 3. Calculated total energies for the 169 possible structures of κ -Al₂O₃ grouped by the Al sites occurring in the first two layers.

TABLE III. The total energies (eV/atom) for unrelaxed structures with stacking sequence $AcBcAbCb$ and varying vacancy positions. The plane-wave cutoff is 650 eV and the k -point set is I.4.

	Structure	E_{tot}
I	$Ac^\alpha Bc^\alpha Ab^\alpha Cb^\alpha$	-284.3742
II	$Ac^\alpha Bc^\beta Ab^\alpha Cb^\gamma$	-283.9871
III	$Ac^\alpha Bc^\gamma Ab^\alpha Cb^\beta$	-283.9871
IV	$Ac^\beta Bc^\alpha Ab^\gamma Cb^\alpha$	-283.9871
V	$Ac^\beta Bc^\beta Ab^\gamma Cb^\gamma$	-283.6279
VI	$Ac^\beta Bc^\gamma Ab^\gamma Cb^\beta$	-283.7318
VII	$Ac^\gamma Bc^\alpha Ab^\beta Cb^\alpha$	-283.9871
VIII	$Ac^\gamma Bc^\beta Ab^\beta Cb^\gamma$	-283.7318
IX	$Ac^\gamma Bc^\gamma Ab^\beta Cb^\beta$	-283.6279

cutoff; (2) for energy differences of the order of 1 eV/atom we can use much cruder k -point samplings and lower plane-wave cutoffs.

IV. RESULTS

We begin by setting up κ - Al_2O_3 structures, with 40 atoms in the supercell, for all 169 different configurations, as defined in Sec. II. The configurations are divided into nine groups (1–9) according to the type (O , T , or M) of the first two Al layers (cf. Table II).

Next, we calculate the total energies of all the 169 configurations using the k set I.2. The results of this calculation, grouped by the layer types, are shown in Fig. 3. The energies for the lowest-energy structure of each group (calculated with k set I.4 and a 650 eV cutoff) are presented in Table II. It is clear that the lowest energy, by a margin of 1.2 eV/atom, is obtained for the group with only O layers. It can also clearly be seen that the energy becomes higher the more tetragonal Al atoms there are in the structures. This calculation shows that the Al sites in κ - Al_2O_3 are octahedral, which confirms the suggestion of Halvarsson, mentioned in Sec. II.

The configurations in the group with the lowest energies,

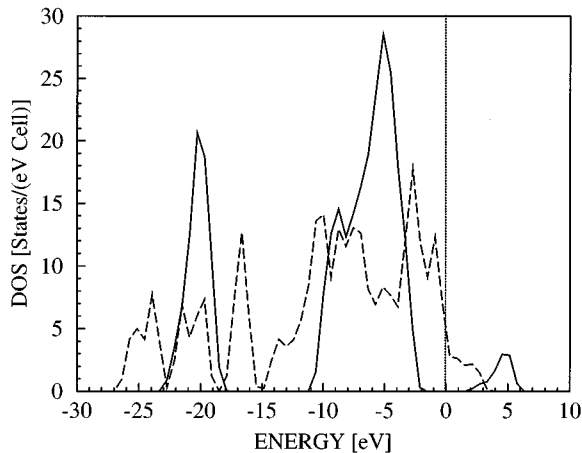


FIG. 4. Calculated total DOS of two different κ - Al_2O_3 structures. The solid line represents a typical structure with Al ions in octahedral positions and the dashed line a typical structure with Al ions in the tetrahedral position.

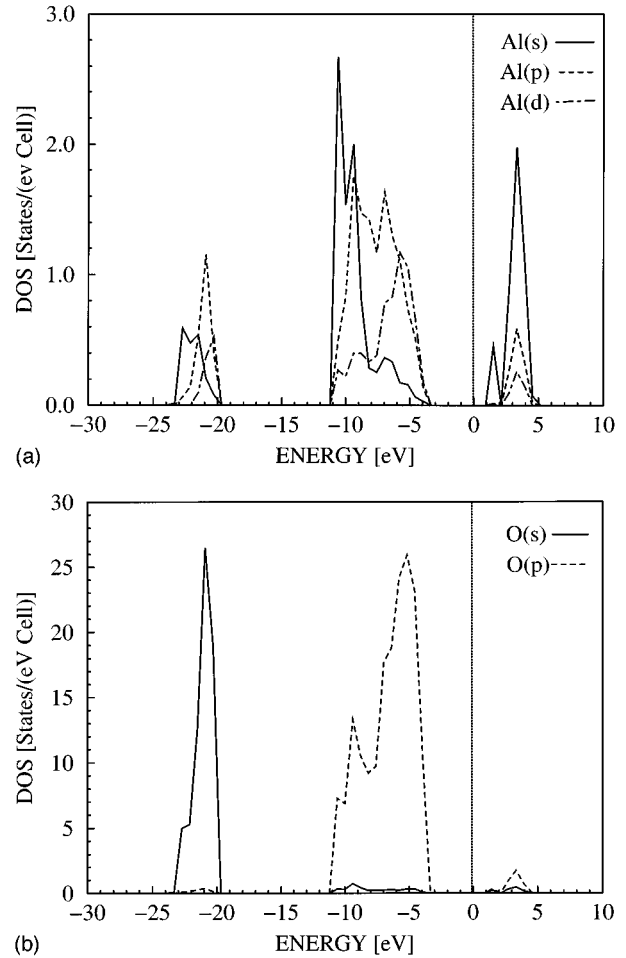


FIG. 5. Calculated orbital-resolved partial DOS of a typical κ - Al_2O_3 structure with Al atoms only in octahedral positions. We project on pseudowave functions truncated at 2 bohrs. Solid, dashed, and long-dashed lines indicate s , p , and d character, respectively.

group 1, have been investigated more carefully. Total-energy results for the nine vacancy configurations (I–IX), differing in their vacancy positions, are listed in Table III. Since we use fixed, ideal coordinates in all our calculations we do not judge the energy differences between these nine configurations large enough to make reliable predictions about their energy ordering. This would require relaxation of the coordinates which is a computational task beyond the scope of this paper.

In the context of accuracy we also make two comments on our use of the LDA as an exchange and correlation functional. First, the lattice constants are usually underestimated by 1–2 % by the LDA. We have ascertained that this does not influence the presented results by repeating some of the calculations with a lattice constant which is 1.5% smaller than the experimental one. In these calculations the structures with tetrahedral Al atoms become even more unfavorable, the more so the more Al atoms that are in tetrahedral sites. Second, recent work on oxides^{26,27} has suggested that it may be necessary to use the generalized-gradient approximation (GGA) instead of the LDA for accurate structural calculations. As the presented effect^{26,27} of the GGA is about 0.1 eV/atom, this is not a problem in the present work since our

energy differences are larger than 1.2 eV/atom. To show this explicitly we include GGA results for some representative structures in Table II.

Our arguments in favor of sixfold coordinated Al atoms in κ -Al₂O₃ are further strengthened by the total density of states (DOS) which we show in Fig. 4 for two configurations. The configuration represented by the solid line has all its Al atoms in octahedral sites. Note that the calculated DOS for the structure with Al atoms in tetrahedral positions shows a metallic character, while it is clear that Al₂O₃ is an insulator and should have a band gap. Quite similar curves are obtained for other configurations with the same Al coordination.

Several studies^{28,29} of the electronic structure of α -Al₂O₃ show that the Al-O bond is highly polar. We confirm that this is the case also for κ -Al₂O₃ by showing in Fig. 5 the orbital resolved partial density of states for a configuration with Al atoms in octahedral positions. Note the different scales used for oxygen and aluminum. Almost all charge can evidently be associated with the oxygen atoms.

V. SUMMARY AND CONCLUSIONS

By accurate total-energy calculations based on the density-functional theory, the local-density approximation,

pseudopotentials, and plane-wave expansions, we show that the stacking sequence of oxygen and aluminum layers in κ -Al₂O₃ is *AcBcAbCb*, implying that all Al atoms are in octahedral positions with coordination number 6. This reduces the number of possible structure models to nine. Our conclusion is based on the fact that the nine remaining structure models are predicted to have significantly lower energy than any other structure model permitted by symmetry, and that the DOS calculations show only these structures to be insulating, in agreement with experiment.

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