Structural and Electronic Properties of Bulk Gibbsite and Gibbsite Surfaces

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Dedicated to Professor Rüdiger Kniep on the Occassion of his 60th Birthday

Abstract. Structure and electronic structure of gibbsite and gibbsite surfaces are studied using gradient-corrected density functional theory and a density-functional based tight-binding (DFTB) scheme. The electronic density-of-states (DOS) is insignificantly changed when comparing bulk and single-layer (001) surfaces, but changes for other surfaces, as pentacoordinated Al sites appear. Model structures of other chemically relevant surfaces are proposed, including a stripe and an $Al_6(OH)_{18}$ cluster model for the (100) face, which turns out to be equivalent to the (011) face if only covalently bound blocks are considered. In all cases quantitative agreement of GGA-DFT and DFTB for structures and occupied electronic states is observed.

Keywords: Aluminum hydroxide; Molecular modelling; Cluster compounds; Density functional calculations; Electronic structure

Introduction

Gibbsite (γ-Al(OH)$_3$) is, together with boehmite (γ-AlOOH) and diaspore (α-AlOOH), one of the main components of bauxite, the raw material for aluminum extraction in the Bayer process [1]. Gibbsite is also used as starting material for production of transition aluminas, which are catalyst supports in refining industry [2]. Moreover, gibbsite is also an important adsorbent for heavy metals making this mineral interesting also from the environmental point of view [3]. In all these cases the surface chemistry of gibbsite plays an important role. Therefore, the mechanism of interaction between adsorbates and the gibbsite surface has attracted much attention. Techniques as EXAFS (extended X-ray absorption fine-structure spectroscopy) and XANES (X-ray absorption near-edge spectroscopy), together with macroscopic evidences of the surface reactivity, are being used to understand the surface processes at the atomistic level [4−8]. Cluster model calculations have also been used to provide new insights on the adsorption processes of this mineral [9]. However, it is not trivial to define a reliable cluster model of gibbsite, and especially the electronic structure of the models has not been discussed in much detail before.

Gibbsite is a sheet structure, usually crystallizing as pseudohexagonal platelets or prisms with monoclinic symmetry. Occasionally, it may also crystallize with triclinic symmetry [10]. The crystal structure is composed of layers of hexacoordinated aluminum atoms, arranged between two layers of hydroxyl groups. Each of these hydroxyl groups is bonded to two aluminum atoms, resulting in electrically neutral sheets which are kept together by (weak) hydrogen bonds, as depicted in figure 3a. *Saafeld* and *Wedde* determined the crystallographic structure for gibbsite by X-ray diffraction [11].

Since there are only hydrogen bonds acting between the layers along the *c* axis, gibbsite exhibits perfect cleavage on the (001) face. Indeed, previous investigations showed that the (001) face is, in fact, the less reactive gibbsite surface with respect to the proton and electrolyte ion adsorption. In this surface the hydroxyl groups are bridged between two Al atoms and have a low proton affinity [12, 13]. Furthermore, *Molis* et al. [14] examined the adsorption of salicylate using adsorption isotherms, electrophoresis, infrared spectroscopy, and controlled rate thermal analysis, providing evidences that the only surface on which there is no adsorption is the (001) one.

They claim that the edge surfaces are more reactive due to the presence of different types of hydroxyl groups (doubly and singly coordinated). In spite of these efforts, no simple model has been proposed for chemical reactions on gibbsite surfaces.

There have been few theoretical atomistic studies on Gibbsite. They include a study of the growing process using interatomic potentials [15], the calculation of the bulk structure and properties using DFT [16, 17], and cluster models studying the adsorption of As(V) complexes [9] and of protons [18] on gibbsite.

Besides these structural studies, there is only little information on electronic properties available in the literature [19]. The creation of clusters, which are suitable for studies of adsorption processes, is not trivial, and detailed investigations of this subject are not available so far. However, it has been shown for similar processes in zeolites that such studies are essential for a correct description of the adsorption mechanism [20].

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In this work we present electronic structure calculations of gibbsite and test different surface models, based on periodic sheets and finite clusters. Special emphasis is given to the change of the electronic structure between the different surface models. We employ DFT computations with a plane-wave basis and an approximate DFT variant, the density-functional based tight-binding (DFTB) method [21, 22]. The latter one will be essential for the study of adsorption processes [23], as it allows computations on significantly larger structures than with full DFT. In fact, there is evidence that large aluminum model clusters are necessary to study the complex adsorption chemistry on gibbsite.

Computational Details

In this study two computational methods based on the density functional theory (DFT) were used. The first is the periodic plane-wave implementation of DFT in the ABINIT software package [24], and the interaction with the ionic core states is described by pseudo potentials [25]. We use the generalized gradient approximation (GGA) for the exchange-correlation potential as proposed by *Perdew*, *Burke* and *Ernzerhof* [26]. The plane wave cutoff energy has been determined by convergence studies, and a value of 36.75 Hartree is found to be sufficient. Details are given in table 1. The second method is the density functional based tight binding method (DFTB) with self-consistent-charge corrections [27]. This method uses a minimal set of atomic basis functions and tight-binding like approximations in the Hamiltonian, and can be applied for periodic and cluster computations. Details on approximation and performance of this method can be found in the literature [21, 22, 27]. The sets of k-points were generated following the procedure of *Pack* and *Monkhorst* [28, 29]. In the Density-of-States (DOS) plots the valence band edge is taken zero point for the energy zero and the levels have been broadened by 0.1 eV.
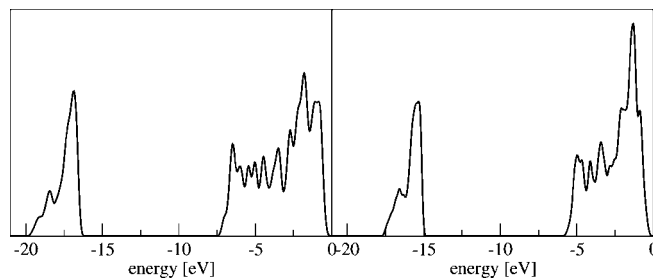

Figure 1 Electronic DOS of α-aluminum oxide calculated with GGA-DFT (left) and DFTB (right).

Test calculations were performed to validate the approximate DFT model on the crystalline structures of α-aluminum oxide (corundum or sapphire) employing experimental geometries [30]. As shown in figure 1, the calculated DOS obtained with the DFTB method is in good agreement with the GGA-DFT calculation, and with data available in the literature [19, 31]. The DFTB valence bands are about 10 % smaller than in GGA-DFT.

Results and Discussion

The structure of gibbsite was calculated with GGA-DFT and DFTB. Full relaxation of the atomic positions gives very similar interatomic distances for both methods. For heavier nuclei (Al and O) these results are in excellent agreement with experiment. Larger differences for the OH bond lengths are due to the poor characterization of proton positions in X-ray experiments. The structure parameters are summarized in table 2. Experimental cell parameters were used in our computations [11] (see table 3). *Digne* et al. included the cell parameters in the optimization and found only minimal changes of the geometry [17]. Indeed, their interatomic distances are very similar to ours, and also the electronic structure (DOS), calculated with experimental and optimized cell parameters show insignificant differences.

Table 1 Convergence test for the total energy difference in Ha for the experimental gibbsite cell with respect to both the plane-wave (PW) energy cutoff and the k-point sampling using the Abinit program using GGA-DFT.

K-point set	PW cutoff energy in Ha 12.25	24.50	36.75	49.00
1 2 1	−400.466	−414.389	−415.346	−415.360
2 4 2	−400.444	−414.387	−415.346	−415.360

Table 3 Applied cell parameters and the k-point meshs for the computation of gibbsite cell and model structures cells.

	Gibbsite	Layer	Stripe	Cluster
a/Å	8.684	8.684	17.368	17.368
b/Å	5.078	5.078	5.078	15.234
c/Å	9.736	9.736	9.736	9.736
β/°	94.54	94.54	94.54	94.54
k-points	2×4×2	2×4×1	1×4×1	1×1×1

Table 2 Experimental and calculated mean atom distances in Å for gibbsite.

	Experimental[a]	Gibbsite crystal cell Calculated[b]	GGA-DFT	DFTB	Layer GGA-DFT	DFTB	Stripe DFTB	Cluster DFTB
Al-Al	2.91	2.93	2.92	2.92	2.94	2.91	2.97	2.99
Al-O	1.89	1.93	1.90	1.89	1.92	1.90	1.89	1.88
O-H	0.83	0.99	0.98	0.96	0.98	0.96	0.96	0.96

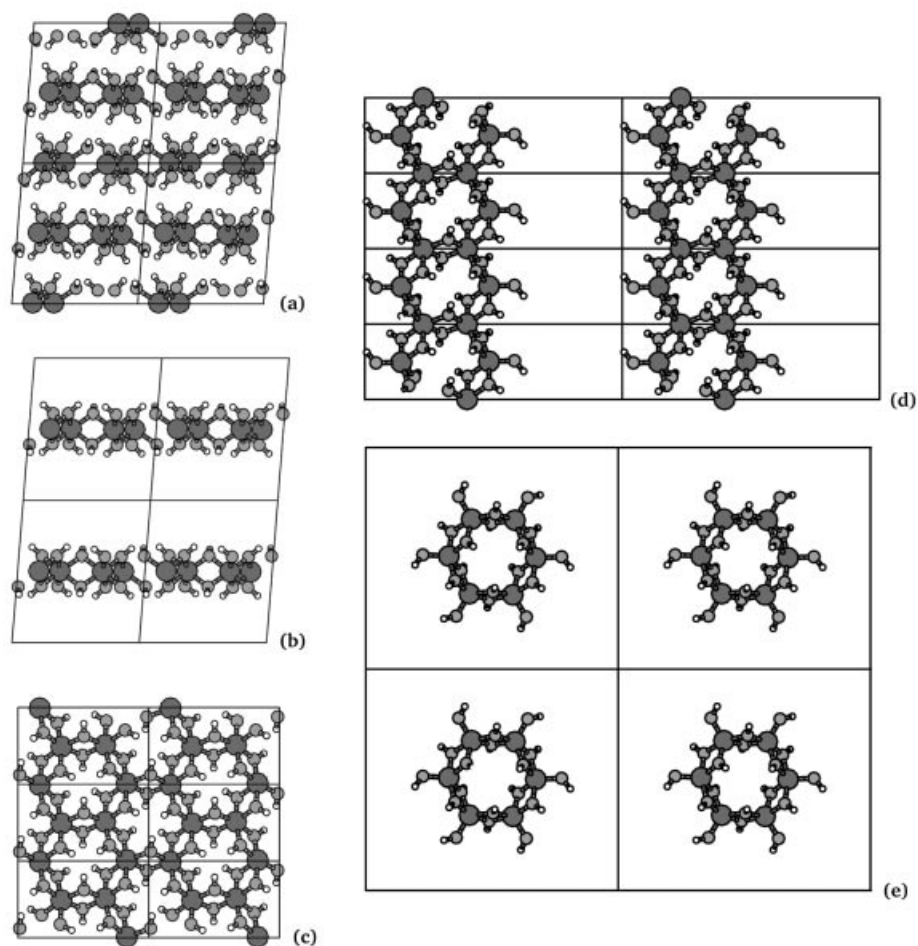[a] *Saalfeld* and *Wedde*, 1974. [b] *Digne* et al., 2002.

Figure 2 a) Four gibbsite unit cells with optimised atom positions. The ac-plane is drawn parallel to the paper. b) Model structure of one gibbsite layer after the removal of the second layer in the unit cell and optimisation of atomic positions. The ac-plane is drawn parallel to the paper. c) The layer model same as in b), but the c-direction is orthogonal to the paper. Six unit cells are depicted. d) The stripe model of gibbsite structure after geometry optimisation, eight unit cells are shown. The a-b plane is parallel to the paper. e) Four unit cells of the gibbsite cluster model $[Al(OH)_3]_6$ with relaxed atomic positions. The paper plane is orthogonal to the c axis.

The DOS of gibbsite is shown in figure 3a. For the GGA-DFT computation, the valence states of the gibbsite spread into two parts, an oxygen 2s band from -20 to -17 eV, and a second one containing oxygen, aluminum and hydrogen valence states from -9 to 0 eV (valence band edge), with a small sub band from -9 to -7 eV. Four main peaks appear at around 5.3, 4.0, 2.0 and 0.9 eV. The relative positions of the upper valence band edge and the 2s oxygen band agree with the XPS study of *Thomas* and *Sherwood* [19]. As can also be seen in figure 3b, the DOS computed with DFTB gives all features as the GGA-DFT. However, quantitatively the band widths are contracted by about 10 %, similar as in the test calculation for α-aluminum oxide discussed above.

In the following, several surfaces of gibbsite, as given in figure 1 by *Sweegers* et al. [10], are studied. First, we constructed a layer model of the (001) surface as shown in figure 2b and 2c. A repeated slab model is created by removing one complete layer in the c-direction from the unit cell. The resulting interlayer distance is sufficiently large (~6 Å), and

the electronic density in between the layers is as low as 10^{-7} electron·Å^{-3}. Obviously, this layer model has the same stoichiometry as the gibbsite bulk. The structure (table 2) and DOS (figure 3) of GGA-DFT and DFTB are matching perfectly. As the interlayer interaction of gibbsite is based only on hydrogen bonds, the DOS of the layer and of the bulk are very similar.

Experimentally, it was found that the (001) surface of gibbsite is practically inert for reactions [12, 13], and the computed DOS further support that there is no strong electronic coupling between the layers. Therefore, when constructing other surfaces, we only include one layer parallel to the (001) direction, which results in stripes (figure 2d). Within this model the (100) and (110) surfaces are identical.

This stripe model has cell parameters as given in table 3. The energetically favored plane in the (100) direction cuts in between two Al atoms, as in this direction the smallest number of covalent bonds are broken. Pairs of OH groups, which are bridging Al atoms, are located in the cutting
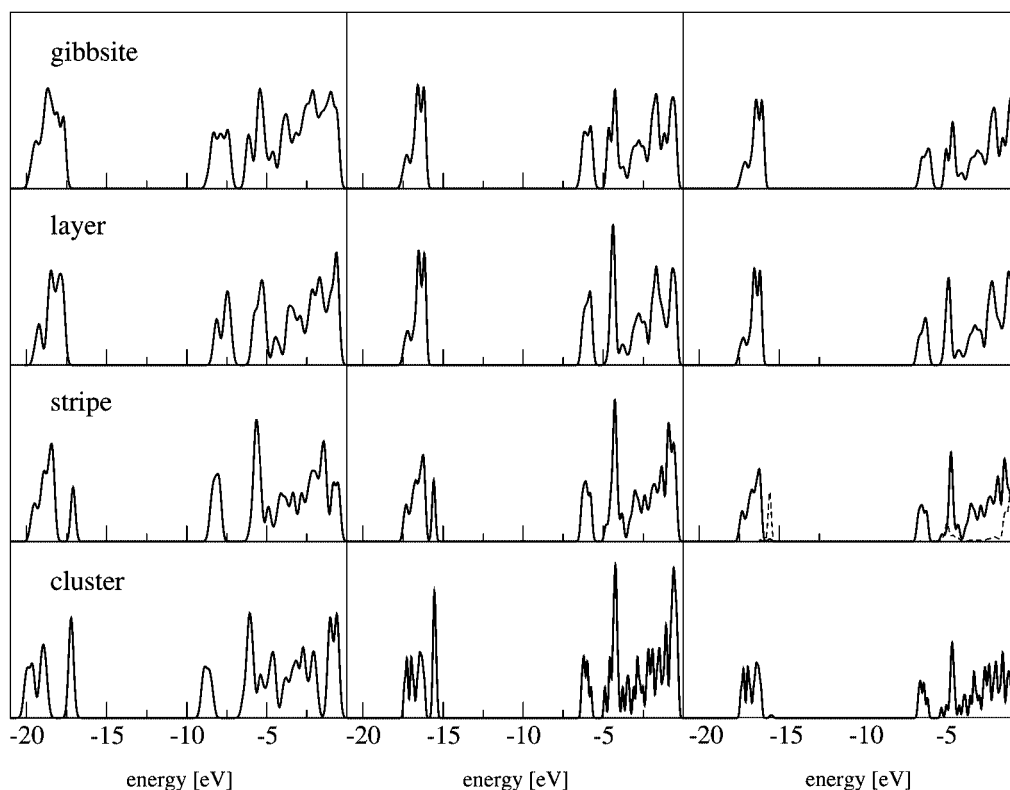
Figure 3 Electronic DOS (arbitrary units) of gibbsite and the surface model structures calculated with DFT a) and DFTB b). In column c) the projected oxygen states (solid curve) and surface oxygen states for the stripe and cluster (dashed curve) are given.

plane. To keep stoichiometry, we include one of these groups on the left, and the inequivalent one on the right side of the stripe. The derived model can alternatively be described as infinite stripe of side linked hexagons [Al(OH)$_3$]$_6$ in the b-direction with two penta-coordinated aluminum per cell at the (100)-surface, one of them on each side of the stripe.

A cluster model can be derived if one shrinks this stripe model also in last infinite dimension. As shown in figure 2e, this hexagonal [Al(OH)$_3$]$_6$ cluster model consists only of penta-coordinated aluminum surface atoms, but still fits the stoichiometry of gibbsite.

The details of the cells for the stripe and the cluster model are given in table 3. For both models the structure parameters are very similar as in the bulk, independent whether GGA-DFT or DFTB are employed. Only the Al-Al distances are 2 % larger, which we attribute to the under coordinated surface aluminum atoms in those models.

Two additional states occur in the DOS of these surface models (figure 3a/b). They are shown in more detail in the projected DOS given in figure 3c. It can be seen that surface hydroxyl oxygen 2*s* states occur at around 1 eV above the gibbsite 2*s* oxygen band, and the hydroxyl oxygen 2*p* states are also shifted by the same energy, hence the latter become the new valence band edge. These features are much stronger pronounced in the cluster, as it contains six Al sur-

Table 4 Mulliken charges derived from DFTB calculation. For the stripe and the cluster model the surface oxygen own a more negative charge, i.e. they bare more basic character.

	Gibbsite	Layer	Stripe	Cluster
Al	0.53	0.51	0.51	–
Al surface	–	–	0.58	0.59
O	−0.44	−0.43	−0.41	−0.40
O surface	–	–	−0.61	−0.60
H	0.26	0.26	0.26	0.26
H surface	–	–	0.28	0.28

face atoms. A cluster model which gives a good description of the electronic structure of the (100) surface needs to be extended to provide the same density of bulk states as the stripe model. Comparing the two methods, also for the DOS, GGA-DFT and DFTB calculations provide similar results for both (100) surface models.

The surface effect can also be seen in the Mulliken atomic charges calculated with the DFTB method (table 4). The charges at the penta-coordinated Al sites are more pronounced. This can be interpreted that the surface increases its basic character. This result is in agreement with the observations of *Hiemstra* et al. [12]. They found that the proton affinity decreases as the (001) surface area increases relative to the other surfaces of the crystal. They also showed that in media with pH below 10, all the faces except the (001) are positively charged (protonated).

Final Remarks

The present study provides a sound basis for perspective studies of chemical reactions on gibbsite surfaces. Periodic models for such reactions are often inappropriate, as it requires to include a large surface to avoid spurious lateral interactions between the substrates. The periodic surface models studied in this work give benchmark values for the structure and the DOS which should be present in meaningful cluster models. The cluster model studied in this work has only surface Al sites and hence misses a large part of the bulk states of gibbsite. The presence of strong polarisation effects within gibbsite and with its environment will also be important in such simulations, but can be included with continuum models or QM/MM techniques at reasonable accuracy. In any case, it is beneficial to be able to compute model structures of reasonably large cluster size, which is possible with the DFTB method. The very good performance of DFTB for gibbsite surfaces, compared to GGA-DFT computations, is encouraging for adsorption studies, as it allows extensive molecular dynamics studies of adsorption processes of large model systems.

This work has twofold conclusions: first, the main characteristics of the electronic structure of the bulk gibbsite are significantly changed when it is reduced to a finite cluster. It is important to note that using the small $Al_6(OH)_{18}$ model cluster, the valence states are significantly different from those of the periodic surface layer, as the cluster consists only of surface atoms. Second, DFTB method gives an equivalent description of the gibbsite structure as well as the model structures for gibbsite surface, compared to GGA-DFT computations. The same trend of electronic band shifts for the gibbsite surface models with respect to the bulk is observed with both methods. We showed that DFTB is a suitable method for the structural and electronic description of gibbsite and gibbsite surfaces. As it provides sufficient accuracy at low computational cost it will be applied to study larger structures and complex chemical processes in our forthcoming work.

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