First-principles study of atomic and electronic structures of kaolinite in soft rock*

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(Received 12 October 2011; revised manuscript received 3 November 2011)

Kaolinite is a kind of clay mineral which often causes large deformations in soft-rock tunnel engineering and thus causes safety issues. To deal with these engineering safety issues, the physical/chemical properties of the kaolinite should be studied from basic viewpoints. By using the density-functional theory, in this paper, the atomic and the electronic structures of the kaolinite are studied within the local-density approximation (LDA). It is found that the kaolinite has a large indirect band gap with the conduction band minimum (CBM) and the valence band maximum (VBM) being at the Γ and the B points, respectively. The chemical bonding between the cation and the oxygen anion in kaolinite is mainly ionic, accompanied by a minor covalent component. It is pointed that the VBM and the CBM of kaolinite consist of oxygen 2p and cation s states, respectively. The bond lengths between different cations and anions, as well as of the different OH groups, are also compared.

Keywords: kaolinite, crystal structure, first-principles method

PACS: 91.60.Ed, 71.15.Mb **DOI:** 10.1088/1674-1056/21/3/039101

1. Introduction

In soft-rock tunnel engineering, one important issue is to deal with large deformations surrounding a soft-rock tunnel. The mechanism of a large deformation is closely related to the interaction between clay minerals and water molecules.[1−3] It is well known that kaolinite is a kind of clay mineral with a perfect 1:1 layer structure constituted by two different surfaces.[4,5] Thus, understanding the interaction of kaolinite and water molecules is one of the main tasks for researchers in the fields of geophysics and geomechanics. To understand the complicated interaction of kaolinite and water molecules, however, one needs to figure out the detailed physical and chemical properties of bulk kaolinite. For this purpose, a comprehensive knowledge of its atomic and electronic structures is required. In contrast to the extensive experimental studies[6−8] that have been carried out in the last decade, up to now, there are very few theoretical works on the atomic and electronic properties of kaolinite.

Motivated by this observation, in this paper, we report a first-principles study of kaolinite by calculating its electronic structure, density of states (DOS), electron charge, and various bond lengths between cations and anions, and of different OH groups. We expect that the present first-principles results (together with those in progress) are helpful to explain the chemical/physical as well as the mechanical behaviors of kaolinite from a microscopic viewpoint.

2. Methods

The kaolinite has a molecular formula of $Al_2Si_2O_9H_4$ with space group $P1$. It is composed of a sheet of corner-sharing SiO_4 tetrahedra and a sheet of edge-sharing AlO_6 octahedra linked by common oxygen atoms parallel to the c axis. The unit cell includes 17 atoms, i.e., two Al atoms, two Si atoms, four hydrogen atoms, and nine oxygen atoms, as shown in Fig. 1. The calculation is based on the density-functional theory (DFT) within the local-density approximation (LDA)[8−11] as implemented in the Vienna *Ab-initio* Simulation Package (VASP)[12,13] code through the use of projector-augmented wave (PAW) pseudopotentials.[14−16] All atomic positions are relaxed according to the calculated Helmann–Feynman forces. The energy cutoff for the plane-wave basis is set at 400 eV. The 2×2×2 Monkhorst–Pack k-point set[17,18] is used to sample the Brillouin zone (BZ). In

*Project supported by the National Natural Science Foundation of China (Grant No. 40972196).

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our calculation, the valence electrons include 3s and 3p of Al, 3s and 3p of Si, 1s of H, and 2s and 2p of O. The optimization of the atomic geometries is performed via a conjugate-gradient algorithm until the residual force acting on the atoms is less than 0.02 eV·Å^{-1}.

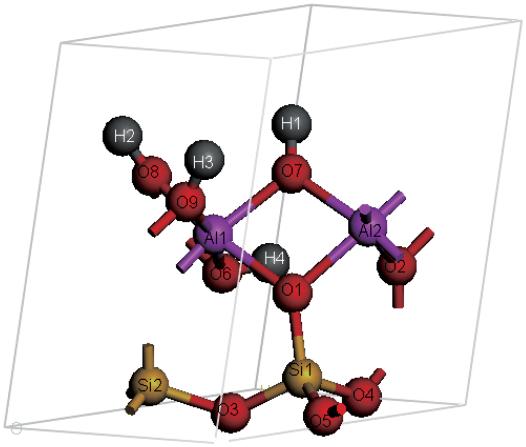


Fig. 1. (colour online) Unit cell of kaolinite $Al_2Si_2O_9H_4$ containing 17 atoms.

3. Results and discussion

Although all the oxygen atoms in kaolinite are inequivalent by symmetry, they can be grouped into four chemically distinct sets. They are the two oxygen atoms (O1 and O2 in Fig. 1) bridging the silicate ring system to the aluminate layer (known as the apical oxygens), the inner oxygen (O6) attached to the inner hydrogen atom, the ring oxygens (O3, O4, O5) that are members of the silicon ring system, and the interlayer oxygens (O7, O8, O9) bonded to the interlayer hydrogens. Table 1 lists the calculated bond lengths in kaolinite. We find that the Si–O (apical) bonds linking to the octahedral aluminium have unusually short bond lengths, while the other Si–O bonds have longer bond lengths. In contrast, the Al–O (apical) bonds have the longest bond lengths, and the Al–O (interlayer) bonds usually have relatively short bond lengths. There are four OH groups in kaolinite, including three interlayer OH groups (O7H1, O8H2, O9H3) and one inner OH group (O6H4). In the optimized structure of kaolinite, the angles of the three interlayer OH groups relative to the (001) plane are 88.11°, 89.92°, and 14.01°, respectively, while the angle of the inner OH group relative to the (001) plane is −6.06°. Considering the bond lengths of these OH groups, we find based on the calculated results that the O–H bonds with relatively long bond lengths of 0.987 Å belong to the OH group that orientates almost perpendicularly to the (001) plane, while the OH groups that orientate almost parallel to the (001) plane have relatively short bond lengths of 0.981 Å. In natural kaolinite, the Al ions of the octahedral sites can be easily substituted by some divalent cations, such as Mg^{2+}. From the calculated results mentioned above, we know that the Al–O bond lengths are longer than the Si–O bond lengths, which means that the Al–O bonds are weaker than the Si–O bonds in strength. This can partially explain why the Al ions in kaolinite can be more easily replaced by some low-valence cations than the Si ions.

Table 1. Calculated bond lengths in the optimized structure of kaolinite.

Bond	Distance/Å	Bond	Distance/Å
Si1–O1	1.607	Si2–O2	1.609
Si1–O3	1.630	Si2–O3	1.634
Si1–O4	1.608	Si2–O4	1.609
Si1–O5	1.635	Si2–O5	1.630
Al1–O1	1.957	Al2–O1	1.970
Al1–O2	1.970	Al2–O2	1.954
Al1–O6	1.908	Al2–O6	1.906
Al1–O7	1.864	Al2–O7	1.874
Al1–O8	1.869	Al2–O8	1.870
Al1–O9	1.869	Al2–O9	1.868
H1–O7	0.987	H3–O9	0.981
H2–O8	0.987	H4–O6	0.981

Figure 2 shows the band structure of kaolinite along the high-symmetry lines of the BZ. The high-symmetry BZ points labeled in Fig. 2 are Γ(0,0,0), B(0.5,0,0), F(0,0.5,0), and G(0,0,0.5). We can see that the conduction-band minimum (CBM) of kaolinite is at the Γ point and the valence-band maximum (VBM) is at the B point. Thus, kaolinite has an indirect band gap with a gap width of 4.89 eV.

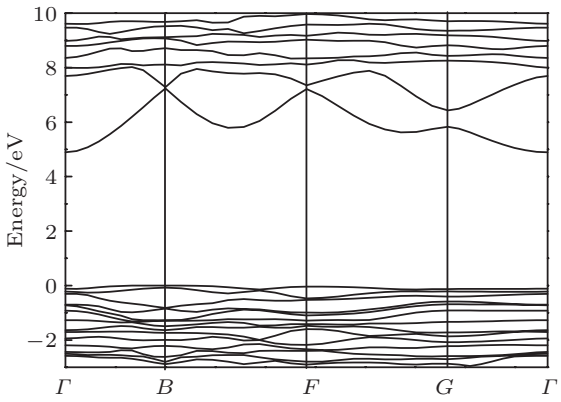


Fig. 2. Band structure of kaolinite along the high-symmetry lines of the Brillouin zone. The Fermi energy is set at zero.

Figure 3 presents the orbital-resolved site-projected densities of states (PDOS) for Al, Si, O, and H atoms (one atom for each atomic component) in a kaolinite unit cell. The Fermi energy E_F has been set at zero. The PDOS of the four different kinds of oxygen atoms are separately plotted in Fig. 3. It is found that the PDOS of the different kinds of oxygen atoms are similar to each other. This similarity is due to the high ionicity of the oxygen, which results in a large charge transfer from the Al 3p, Si 3p, and H 1s states to the O 2p states. In fact, we can see from Fig. 3 that the valence bands in the wide energy range of -10 eV$<E<E_F$ are mainly composed of the O 2p states. On the other hand, it is revealed in Fig. 3 that there are some residual charge in the Al 3s/3p and the Si 3s/3p states, which implies that there are also observable covalent components in the Al–O and the Si–O chemical bondings in kaolinite. This mixed ionic/covalent bonding character is reminiscent of the cases in Al_2O_3 and SiO_2 binary compounds, in which the cation–anion chemical bonding also displays both ionic and covalent components with the latter dominating the bond.

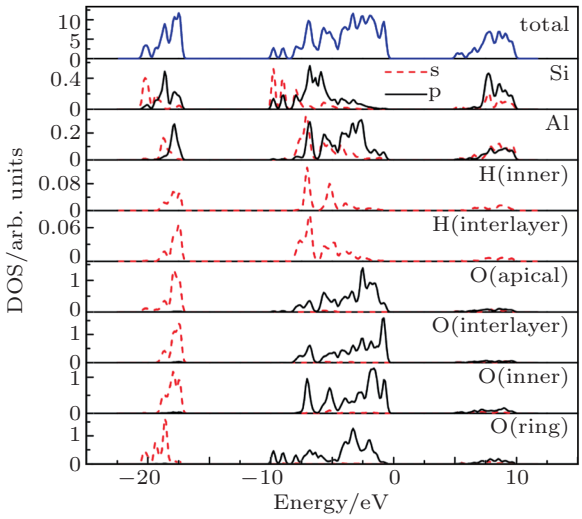


Fig. 3. (colour online) Orbital-resolved partial DOS for Si, Al, O, and H atoms (from top to bottom) in a kaolinite unit cell. The Fermi energy is set at zero. The total DOS is plotted at the top most panel.

Table 2. Calculated orbital-decomposed site(atom)-projected electron charge inside the muffin-tin spheres of kaolinite at the high-symmetry BZ points.

State	Site	s	p	State	Site	s	p
Γ(v)	O(apical)	0.0	0.013	F(v)	O(apical)	0.0	0.020
	O(ring)	0.0	0.0		O(ring)	0.0	0.004
	O(inner)	0.0	0.031		O(inner)	0.0	0.180
	O(interlayer)	0.0	0.265		O(interlayer)	0.001	0.115
	H(interlayer)	0.0	0.0		H(interlayer)	0.0	0.0
	H(inner)	0.0	0.0		H(inner)	0.0	0.0
	Al	0.0	0.013		Al	0.0	0.005
	Si	0.0	0.001		Si	0.0	0.0
Γ(c)	O(apical)	0.023	0.002	F(c)	O(apical)	0.011	0.038
	O(ring)	0.028	0.02		O(ring)	0.036	0.013
	O(inner)	0.025	0.007		O(inner)	0.007	0.047
	O(interlayer)	0.018	0.02		O(interlayer)	0.005	0.014
	H(interlayer)	0.001	0.0		H(interlayer)	0.001	0.0
	H(inner)	0.001	0.0		H(inner)	0.002	0.0
	Al	0.029	0.0		Al	0.004	0.011
	Si	0.023	0.0		Si	0.022	0.044
B(v)	O(apical)	0.0	0.018	G(v)	O(apical)	0.0	0.008
	O(ring)	0.0	0.001		O(ring)	0.0	0.001
	O(inner)	0.0	0.02		O(inner)	0.0	0.026
	O(interlayer)	0.002	0.305		O(interlayer)	0.0	0.265
	H(interlayer)	0.0	0.0		H(interlayer)	0.0	0.0
	H(inner)	0.0	0.0		H(inner)	0.0	0.0
	Al	0.001	0.006		Al	0.0	0.012
	Si	0.0	0.001		Si	0.0	0.001
B(c)	O(apical)	0.020	0.015	G(c)	O(apical)	0.017	0.013
	O(ring)	0.0	0.030		O(ring)	0.041	0.004
	O(inner)	0.0	0.019		O(inner)	0.023	0.030
	O(interlayer)	0.017	0.013		O(interlayer)	0.0	0.014
	H(interlayer)	0.002	0.001		H(interlayer)	0.0	0.0
	H(inner)	0.0	0.0		H(inner)	0.002	0.0
	Al	0.010	0.008		Al	0.005	0.009
	Si	0.034	0.017		Si	0.031	0.003

To obtain more precise information about the charge distribution among the different atomic elements in kaolinite, we calculate the orbital-decomposed band charge inside the muffin-tin spheres of kaolinite at VBM and CBM at high-symmetry BZ points Γ, B, F, and G. The result is listed in Table 2. Taking Γ and B points for example, we can see from Table 2 that the CBMs at Γ (denoted by Γ(c) in Table 2) and B (B(c)) points consist of the cation s (3s for Al and Si, 1s for H) states with slight oxygens s states. Whereas, the VBMs at Γ (Γ(v)) and B (B(v)) points consist mainly of O 2p states, especially, the O(interlayer) 2p states. The orbital charge features at F and G points are similar to those at B and Γ points. Physically, Al and Si atomic 3s levels are higher than O atomic 2p level, thus, the VBM of kaolinite mainly consists of oxygen 2p states, while the CBM is mainly characterized by the cation s states.

4. Conclusion

In summary, we have studied the atomic and the electronic structures of kaolinite through first-principles DFT-LDA calculations. The calculation shows that the Al–O bond lengths are longer than the Si–O bond lengths, and the bond lengths of the OH groups that orientate perpendicularly to the (001) plane are longer than those of the OH groups that orientate parallel to the (001) plane. It has been found that the CBM of kaolinite is at the Γ point and the VBM is at the B point. The calculated indirect band gap is 4.89 eV. Our analysis of the PDOS has shown that the chemical bonds between the cations and the oxygen anions in kaolinite are mainly ionic accompanied by minor covalent components. The band-charge analysis shows that the VBM consists of oxygen 2p states and the CBM consists of cation and oxygen s states. The present calculated results for bulk kaolinite serve to understand the chemical and the physical properties of a kaolinite surface and its interaction with water molecules, which plays a key role in the large deformations found in soft-rock tunnels.

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