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Atomic and electronic structures of montmorillonite in soft rock*

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Montmorillonite is a kind of clay mineral which often causes large deformation in soft-rock tunnel engineering and thus brings about safety problems in practice. To deal with these engineering safety problems, the physical and chemical properties of montmorillonite should be studied from basic viewpoints. We study the atomic and electronic structures of montmorillonite by using density-functional theory within the local-density approximation (LDA). The results of calculation show that Al–O bond lengths are longer than Si–O bond lengths. It is found that both the valence band maximum (VBM) and the conduction band minimum (CBM) of montmorillonite are at point Γ, and the calculated direct band gap of montmorillonite is 5.35 eV. We show that the chemical bonding between cations and oxygen anions in montmorillonite is mainly ionic, accompanied as well by a minor covalent component. It is pointed out that the VBM and CBM of montmorillonite consist of oxygen 2p and cation s states, respectively. Our calculated results help to understand the chemical and physical properties of montmorillonite, and are expected to be a guide for solving the problem of large deformation of soft-rock tunnels.

Keywords: montmorillonite, electronic structure, first-principles method
PACC: 7115A, 8607C, 9160W

1. Introduction

In soft-rock tunnel engineering, one important issue is how to deal with the large deformation in surroundings of the soft-rock tunnel. The mechanism of this large deformation is closely related to the interaction between the clay mineral and the water molecules.[1,2] It is well known that montmorillonite is a kind of clay mineral with a 2:1 layer structrue.[3,4] Thus, the understanding of the interaction of the montmorillonite and the water molecules is one of the main tasks for researchers in both the fields of geophysics and geomechanics. To understand the complicated interaction of the bulk montmorillonite and water molecules, however, one needs to work out the detailed physical and chemical properties of the bulk montmorillonite. For this purpose, a comprehensive knowledge of atomic and electronic structures are necessarily required.

Many experiments have been performed to investigate the chemical and physical properties of montmorillonite, Gong *et al*[5] found that the state and quantity of absorbed water in montmorillonite depend on the hydration capability and quantity of exchangeable cations in montmorillonite. Some researchers have also studied the conductance properties of high-valence ions in montmorillonite, showing that montmorillonite is a practical and promising solid electrolyte material.[6,7] These experimental studies discovered the chemical and physical properties of montmorillonite, however they cannot tell us the atomic and electronic properties of montmorillonite.

In addition, in contrast to these extensive experimental studies that have been carried out in the last decade, up to now there have been very few theoretical works on atomic and electronic properties of the montmorillonite. In particular, we notice that an *ab initio* investigation of montmorillonite is still lacking. Motivated by this observation, in this paper we report a series of first-principles studies of the montmorillonite by calculating its electronic structure, density of states

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(DOS), electron charges, and various bond lengths between the cations and anions and of OH groups in montmorillonite. We expect that the present first-principles results (together with those in progress) are helpful in explaining the various chemical/physical as well as the mechanical behaviors of montmorillonite from a microscopic perspective.

2. Methods

Montmorillonite belongs to the space group of $C2/m$,[8] it is a kind of clay mineral made up of a layer of octahedral aluminium oxides between two layers of tetrahedral silicium oxides; the crystal structure of montmorillonite is shown in Fig.1. In the present study we construct a montmorillonite calculation model with an ideal formula $Al_2Si_4O_{12}H_2$.[8] The unit cell used in calculating the electronic structure includes 20 atoms, i.e., two Al atoms, four Si atoms, two hydrogen atoms, and twelve oxygen atoms. The calculated structural parameters are: $a = 5.208$ Å, $b = 9.020$ Å and $c = 10.13$ Å.[9] Our calculations for the montmorillonite are based on density-functional theory (DFT) within the local-density approximation[10] as implemented in the vienna ab-initio simulation package (VASP)[11] code through the use of the projector augmented wave (PAW) pseudopotentials.[12] All atomic positions were relaxed according to the calculated Helmann–Feynman forces. The energy cutoff for the plane-wave basis was 400 eV. The $2 \times 2 \times 2$ Monkhorst–Pack k-point set[13,14] was used to sample the Brillouin zone. In our calculation, the valence electrons include 3s and 3p of Al, 3s and 3p of Si, 1s of H, 2s and 2p electrons of O. The optimization of atomic geometries was performed via a conjugate-gradient algorithm until residual force acting on atoms was less than 0.01 eV $\cdot$ Å^{-1}.

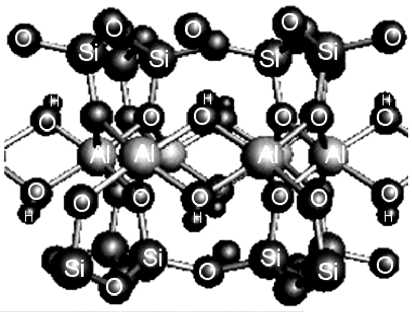


Fig.1. The crystal structure of the montmorillonite.

3. Results and discussion

Table 1 lists the calculated bond distances in montmorillonite. In montmorillonite, oxygen atoms in crystal structure are inequivalent in symmetry. In fact, there are three different kinds of local coordinates for oxygen atoms: i.e., the oxygen atoms bridging the silicon ring to the aluminium layer, labeled as apical oxygens; the inner oxygen atoms attaching to the inner hydrogen atom as well as aluminium atom; and the ring oxygens which are members of the silicon rings in montmorillonite. From the calculated results, Si–O (apical) bond lengths are slightly longer than Si–O (ring) bond lengths; a similar trend can be found that Al–O (apical) bonds also have the slightly longer lengths than Al–O (inner) bonds. These two combined facts show that the cation–anion bonds along the c axis are weaker than those in the a-b plane, which can be partially used to explain why the large lattice deformation observed in montmorillonite is always along the c axis.

Table 1. The calculated bond lengths in optimized structure of montmorillonite.

bonds	calculated bond distances/Å
Si–O(apical)	1.634
Si–O(ring)	1.619
Al–O(apical)	1.913
Al–O(inner)	1.904
H–O(inner)	0.978

According to Ref.[15], in natural montmorillonite the Al^{3+} ions of the octahedral sites can be easily substituted by some divalent cations such as Mg^{2+}, which leads to residual negative charges in montmorillonite, which are in turn compensated for by interlayer counter cations such as Na^+, K^+ or Cs^{2+}. These counter cations are directly responsible for adsorption of large amounts of water molecules, which will result in a large deformation of montmorillonite. From Table 1 one can see that the Al–O bond lengths are longer than the Si–O bond lengths, which means that the Al–O bonds are weaker in strength than the Si–O bonds. This can partially explain why Al ions in montmorillonite are easier than Si ions to be replaced by some low-valent cations. We also found that the hydrogen atoms inside the montmorillonite form O–H bonds with an O–H bond length of 0.978 Å, and the equilibrium position of inner O–H bond is parallel to the a-b plane (forming an angle of 29.01°).

Figure 2(a) shows the band structure of montmorillonite along the high-symmetry lines in the Brillouin zone (BZ). The high-symmetry BZ points labeled in Fig.2(a) are Γ (0,0,0), A $(-0.5, 0, 0)$, L $(0.5, 0, 0.5)$, M $(-0.5, -0.5, 0.5)$, Z $(0, -0.5, 0.5)$ and V $(0, 0, 0.5)$. As shown in the Fig.2(a), one can see that both the conduction-band minimum (CBM) and the valence-band maximum (VBM) of the montmorillonite are at the Γ point. Thus, the montmorillonite has a direct gap with a value of 5.35 eV, which means the simple montmorillonite is an insulator. Figure 2(b) shows the band structure of Mg-montmorillonite along the same high-symmetry lines in the Brillouin zone (BZ). From Fig.2(b), we can find that in the band structure of Mg-montmorillonite, the impurity band appears nearest to the top of the valence band, which can introduce the negative charge in montmorillonite. This impurity band level results mainly from the Mg atom substitute for the Al atoms in montmorillonite. According to the experimental studies,[6,7,15] the substituting Mg atom can introduce negative charge in montmorillonite, which can be well explained by our calculated results.

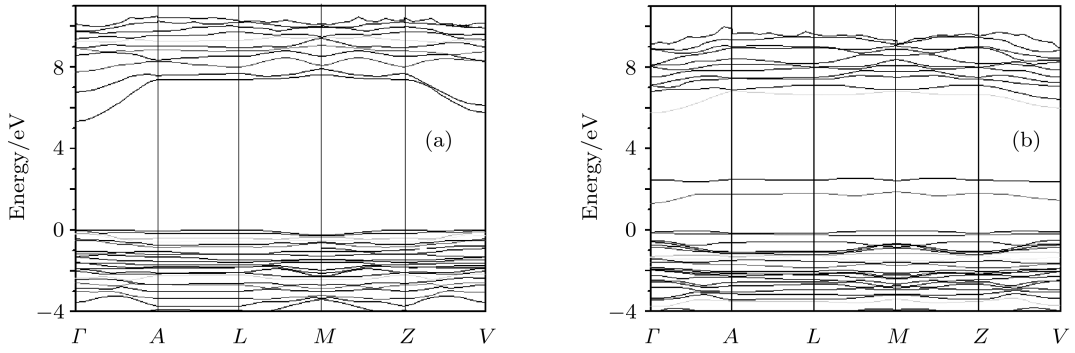


Fig.2. (a) The band structures of montmorillonite along the high-symmetry directions, energy zero is set to E_{VBM}. (b) The band structures of Mg-montmorillonite along the high-symmetry directions.

Figure 3 presents the orbital-resolved site-projected density of states (PDOS) for Al, Si, O, and H atoms (one atom for each atomic component) in the montmorillonite unit cell. The Fermi energy E_{F} has been set at zero. Because of the different symmetries and positions, the PDOS of the three different kinds of oxygen atoms are separately plotted in Fig.3. It is found that the PDOS of different kinds of oxygen atoms are similar to each other. This similarity is due to the high ionicity of 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, one can see from Fig.3 that the valent bands in a wide energy range -10 eV $< E < E_{\mathrm{F}}$ are largely composed of O 2p states. On the other hand, Fig.3 reveals that there are some residual charges in the Al 3s/3p and Si 3s/3p states, which implies that there is also an observable covalent component in Al–O and Si–O chemical bonding in montmorillonite. Figure 4 presents the total crystal charge density sampled in the plane containing the silicon

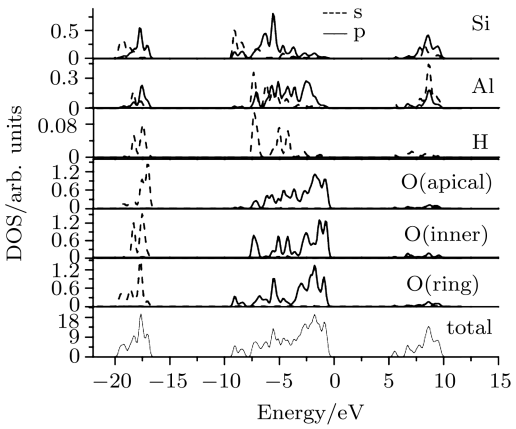


Fig.3. The density of states of montmorillonite. Energy zero is set to E_{VBM}. The bottom panel shows the total DOS of the montmorillonite, others show the DOS of the s and p orbitals in the four component atoms.

atom and the apical oxygen atom. Accordingly, from the charge density of Si and Al atoms shown in Fig.4, we also confirm the above conclusions. This mixed ionic/covalent bonding character is reminiscence of

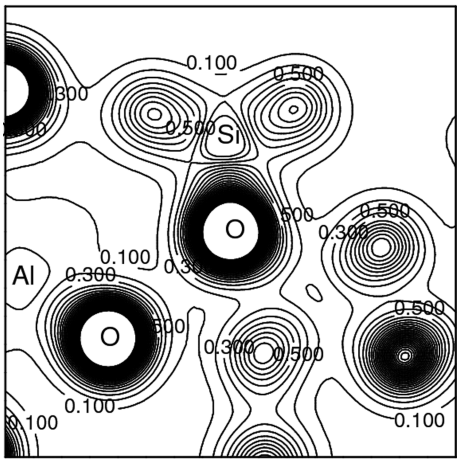


Fig.4. Total crystal charge density sampled in the plane contain the silicon atom and the apical oxygen atom.

cases in binary compounds Al_2O_3 and SiO_2, in which the cation-anion chemical bonding also displays both ionic and covalent components with the latter more dominant than the former.

To obtain a more precise knowledge of charge distribution among the different atomic elements in montmorillonite, furthermore, we have calculated the orbital-decomposed band charges inside the muffin-tin spheres of montmorillonite at VBM and CBM at high-symmetry BZ points. The result is listed in Table 2. Taking the Γ point as an example, one can see from Table 1 that the CBM at Γ (denoted by Γ (c) in Table 1) consists mainly of the cation s states and some O atom s (3s for Al and Si, 1s for H and 2s for O) states. Whereas, the VBM at Γ (Γ(v)) consists mainly of O 2p states, especially, O(apical) 2p states. The orbital charge features at other points are similar to those at Γ points. Physically, Al and Si atomic 3s levels are higher than O atomic 2p level, thus, the VBM of montmorillonite mainly consists of oxygen 2p states, while the CBM is mainly characterized by cation s states.

Table 2. calculated l-decomposed electron charges inside the muffin-tin spheres of montmorillonite at the all high-symmetry points.

states	site	s	p	states	site	s	p
Γ(v)	H(inner)	0.000	0.000	M(v)	H(inner)	0.000	0.000
	O(apical)	0.000	0.119		O(apical)	0.000	0.001
	O(inner)	0.000	0.007		O(inner)	0.001	0.055
	O(ring)	0.000	0.028		O(ring)	0.000	0.209
	Al	0.000	0.000		Al	0.000	0.010
	Si	0.001	0.001		Si	0.000	0.003
Γ(c)	H(inner)	0.001	0.001	M(c)	H(inner)	0.007	0.001
	O(apical)	0.015	0.001		O(apical)	0.000	0.013
	O(inner)	0.016	0.000		O(inner)	0.002	0.025
	O(ring)	0.021	0.004		O(ring)	0.028	0.021
	Al	0.029	0.000		Al	0.008	0.005
	Si	0.015	0.001		Si	0.001	0.001
A(v)	H(inner)	0.000	0.000	L(v)	H(inner)	0.000	0.000
	O(apical)	0.000	0.003		O(apical)	0.000	0.003
	O(inner)	0.000	0.066		O(inner)	0.000	0.060
	O(ring)	0.000	0.178		O(ring)	0.000	0.170
	Al	0.000	0.005		Al	0.000	0.005
	Si	0.000	0.002		Si	0.000	0.002
A(c)	H(inner)	0.001	0.0001	L(c)	H(inner)	0.003	0.001
	O(apical)	0.001	0.012		O(apical)	0.001	0.010
	O(inner)	0.002	0.022		O(inner)	0.001	0.015
	O(ring)	0.004	0.028		O(ring)	0.009	0.018
	Al	0.000	0.003		Al	0.002	0.004
	Si	0.014	0.011		Si	0.009	0.014
Z(v)	H(inner)	0.000	0.000	V(v)	H(inner)	0.000	0.000

Table 2 (*Continued*)

states	site	s	p	states	site	s	p
	O(apical)	0.000	0.029		O(apical)	0.000	0.124
	O(inner)	0.000	0.068		O(inner)	0.000	0.004
	O(ring)	0.000	0.170		O(ring)	0.000	0.020
	Al	0.000	0.005		Al	0.000	0.000
	Si	0.000	0.001		Si	0.001	0.001
Z(c)	H(inner)	0.003	0.001	V(c)	H(inner)	0.002	0.001
	O(apical)	0.015	0.007		O(apical)	0.010	0.007
	O(inner)	0.001	0.007		O(inner)	0.019	0.000
	O(ring)	0.009	0.018		O(ring)	0.028	0.006
	Al	0.002	0.004		Al	0.038	0.000
	Si	0.011	0.020		Si	0.013	0.001

4. Summary

We have studied the atomic and electronic structures of montmorillonite through first-principles DFT-LDA calculations. It has been found that both the CBM and the VBM of montmorillonite are at the Γ point. The calculated direct band gap is 5.35 eV. Our analysis of the electron PDOS has shown that the dominant chemical bonding component between cations and oxygen anions in montmorillonite is ionic, which is accompanied by a minor covalent component. The band-charge analysis has shown that the VBM and CBM of montmorillonite mainly consist of oxygen 2p and cation s states, respectively. The present calculated results for bulk montmorillonite serves as the first step to understanding the chemical and physical properties of montmorillonite surface and its interaction with water molecules, which plays a key role in large deformation of soft-rock tunnels.

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