Pressure dependence of the electronic structure in kaolinite: A first-principles study

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Using the first-principle methods, the pressure dependence of the electronic structure and band structure of kaolinite were studied within the local-density approximation. The calculated results show that pressure would chiefly alter the band structure of kaolinite, while pressure can have its main effect on the band gap of kaolinite. At $p = 0.6$ GPa, band structure of kaolinite first converts an indirect gap into a direct gap, and then recovers an indirect gap structure at $p = 66.2$ GPa because CBM shift in the band structure is under high-pressure. The bond Si–O is more stable than bond Al–O under pressure, in addition, pressure has a significant effect on the inner hydroxyl bond of kaolinite and leads to a large variation of H–O(inner) bond lengths. The calculated results will not only help to understand the electronic structure of kaolinite under pressure, but also provide theoretical guidance for deal with the safe problems of soft-rock tunnel engineering.

Keywords: First-principles method; pressure; kaolinite.

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1. Introduction

Pressure is continually gaining more importance in soft-rock tunnel engineering, because of increasing mining depth and intensity, deep mining process due to high ground stress, high geothermal, high Karst water pressure and mining exploitation, which often cause the problems of soft-rock tunnel engineering and safety accidents in engineering practice.^{1,2} The engineering problem in soft-rock tunnel has increased

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the demands for the better understanding of clay materials under pressure.^{3,4} In addition, the understanding of the pressure properties of the clays is also one main task for the researchers in both fields of geophysics and geomechanics. Among clay minerals, kaolinites have been extensively investigated because of not only their great technological importance in soft-rock tunnel engineering application, but also their interesting rich physical and chemical properties from the basic theoretical viewpoint.^{5–7} Many of the engineering safety problems are related to the pressure dependence of the properties of kaolinite. This is due to the fact that kaolinite has a kind of clay minerals with perfect 1:1 layer structure constituted by two different surfaces. For finite size, it is well known that high-pressure leads to more closely packed structure, which provides a way to alter the atomic and electronic structure in kaolinite. Thus, studying the pressure dependence of electronic structure and band structure is one of the most important topics in kaolinite research.

During the past decade, a large number of studies^{8–15} on the physical and chemical properties of kaolinite have been performed. Nisar *et al.* studied the Optical gap and native point defects in kaolinite.⁸ Then, Welch *et al.* investigated the high-pressure behavior of kaolinite.⁹ Recently, Etienne *et al.* tested the pore size and responses of kaolinite with different structures.¹⁰ In contrast to the extensive experimental studies that have been carried out in the last decade, however, up to now, there have been very few theoretical works studying the physical and chemical properties of kaolinite.^{8,16,17} In particular, an *ab initio* investigation of pressure properties of kaolinite is still lacking. Furthermore, it is worthwhile to introduce the theoretical work to explain the pressure properties of kaolinite from the basic viewpoints. Motivated by this observation, in this paper, a series of first-principles study pressure properties of kaolinite was reported by calculating its electronic structure, bond lengths, and density of states (DOS). The present first-principles results may be used to give a useful guide not only for the basic research on kaolinite, but also for the future technological applications of soft-rock tunnel engineering.

2. Methods

The kaolinite is an aqueous silicate mineral, in which water is present in the form of hydroxyl groups with molecular formula $\text{Al}_2\text{Si}_2\text{O}_9\text{H}_4$.¹⁷ It is composed of a sheet of corner-sharing SiO_4 tetrahedra linked, by common oxygen atoms parallel to the *c*-axis, to a sheet of edge-sharing AlO_6 octahedra. The unit cell used in calculating the electronic structure includes 17 atoms, i.e. two Al atoms, two Si atoms, four hydrogen atoms and nine oxygen atoms (as shown in Fig. 1). The calculations for the kaolinite are based on density functional theory (DFT) within the local-density approximation (LDA)^{18,19} as implemented in the vienna *ab initio* simulation package (VASP)^{20,21} code through the use of the projector augmented wave (PAW) pseudopotentials.^{22,23} All atomic positions are relaxed according to the calculated Hellmann–Feynman force. Energy cutoff for the wave plan is set to 500 eV. The Monkhorst–Pack *k*-point is set to $5 \times 5 \times 5$ ^{24,25} and is used to sample the Brillouin

Fig. 1. (Color online) Unit cell of the kaolinite $\text{Al}_2\text{Si}_2\text{O}_9\text{H}_4$ containing 17 atoms, the red atoms are O atoms, the purple atoms are Al atoms, the yellow atoms are Si atoms, the gray atoms are H atoms.

zone. $3s$ and $3p$ of Al, $3s$ and $3p$ of Si, $1s$ of H, $2s$ and $2p$ electrons of O are considered to be valence electrons in our calculation. The optimization of atomic geometries was performed via a conjugate gradient algorithm until residual force acting on atoms was less than $0.01 \text{ eV } \text{\AA}^{-1}$. The calculated structural parameters are $a = 5.160(5.155) \text{ \AA}$, $b = 5.160(5.155) \text{ \AA}$, $c = 7.602(7.405) \text{ \AA}$, compared with the available experimental data in parentheses.²⁶

3. Results and Discussion

Table 1 lists the calculated bond lengths in kaolinite under different pressures. In kaolinite, all oxygen atoms in crystal structure are inequivalent by symmetry, note that there are four different kinds of local coordinates for oxygen atoms, i.e. there are two oxygen atoms (O_1 , O_2) bridging the silicon ring system to the aluminium layer labeled as apical oxygens; the ring oxygens (O_3 , O_4 , O_5), which are members of the silicon ring system; the inner oxygen (O_6), which is attached to the inner hydrogen atom; and the interlayer oxygens (O_7 , O_8 , O_9), bonded to the interlayer hydrogens. From Table 1, at $p = 0 \text{ GPa}$, Si–O(ring) bond lengths are slightly longer than Si–O(apical) bond lengths. Furthermore, it is obvious that Al–O(apical) bond lengths are longer than the Al–O(inner) and Al–O(interlayer). It is well known that external pressure will push packed 1:1 layer structure, which will have a large effect on volume and lead to some obvious changes in bond lengths. As a result, one can see that, the inner Al–O(apical) bond lengths significantly decrease from $1.96 \text{ \AA}$ to $1.70 \text{ \AA}$ with pressure increases, the similar trend can also be found for Al–O(inner)

Table 1. The pressure dependence of the calculated bond lengths in optimized structure of kaolinite.

Bonds	0 GPa bond lengths (Å)	20 GPa bond lengths (Å)	40 GPa bond lengths (Å)	60 GPa bond lengths (Å)	80 GPa bond lengths (Å)	100 GPa bond lengths (Å)
Si-O _{apical}	1.60	1.65	1.65	1.64	1.70	1.67
Si-O _{ring}	1.63	1.62	1.61	1.59	1.55	1.55
Al-O _{apical}	1.96	1.82	1.79	1.77	1.74	1.70
Al-O _{inner}	1.90	1.79	1.75	1.73	1.76	1.73
Al-O _{interlayer}	1.86	1.88	1.86	1.83	1.74	1.72
H-O _{interlayer}	0.99	0.99	1.00	1.00	1.06	1.08
H-O _{inner}	0.98	0.99	0.99	0.99	1.06	1.42

and Al-O(interlayer). However, for bond Si-O(ring) and Si-O(apical), which relate to silicon ring system, their bond lengths are slightly changing. Considering the lengths of hydroxyl groups, the calculation results have shown that, for H-O(inner), the sharp increase of bond lengths (from 0.98 Å to 1.42 Å) as the pressure increases from 0 GPa to 100 GPa indicates that pressure has a large effect on the inner hydroxyl bond of kaolinite and leads to a large variation of H-O(inner) bond lengths. From the calculated results above, the Al-O bond length is longer than the Si-O bond length, the lengths of Al-O bond became shorter significantly with the increase of pressure; whereas the bond lengths of Si-O and H-O band have relatively small change. These results indicate that bond Si-O is more stable than bond Al-O under pressure. It can partially explain the reason that Al ions in kaolinite are easily replaced by some low-valent cation than Si ions.

Figure 2 shows the band structure of kaolinite under different pressures. The high-symmetry BZ points include $\Gamma(0, 0, 0)$, $\mathbf{B}(0.5, 0, 0)$, $\mathbf{F}(0, 0.5, 0)$ and $\mathbf{G}(0, 0, 0.5)$ which are marked in Fig. 2. Results for other pressure are also calculated; this paper does not list them here for the sake of conciseness. At $p = 0$ GPa (see Fig. 2(a)), the valence-band maximum (VBM) of the kaolinite is at the $\mathbf{B}$ point and the conduction-band minimum (CBM) is at the Γ point, which shows that kaolinite has an indirect band gap with the gap width of 5.08 eV. Note that in Figs. 2(b)–2(d), the band gap is now direct with both VBM and CBM at the Γ point, whereas in Figs. 2(e) and 2(f), the band gap is indirect with VBM at the $\mathbf{B}$ point. These results indicate that the pressure would chiefly alter the conduct band structure of kaolinite. With increasing pressure, the shape of valence band remains similar, whereas the shape of conduct band has some changes because of the shifting up of conduction band.

In order to further understand these indirect-to-direct and direct-to-indirect band gap transitions, Table 2 lists the VBM and CBM for high-symmetry BZ points in kaolinite. Figure 3 also shows the energy of VBM and CBM as a function of the pressure for each high symmetric K point. One interesting result shows that the band structure of kaolinite is converting an indirect gap into a direct gap under tiny pressure, while the high-pressure could also change the band structure of kaolinite

Fig. 2. (Color online) The change of band structure as functions of pressure for kaolinite. Band structure along the high-symmetry lines in the Brillouin zone. The Fermi energy is set at zero. (a), (b), (c), (d), (e) and (f) represent the pressure values of 0 Gpa, 20 Gpa, 40 Gpa, 60 Gpa, 80 Gpa and 100 Gpa, respectively.

from a direct band gap to an indirect band gap. Comparing Fig. 2 with the data in Table 2, under pressure ranging from 0 GPa to 0.5 GPa, one sees that kaolinite keeps the indirect gap, in which VBM is at **B** point and CBM at Γ point. When $p = 0.6$ GPa, VBM changes from **B** point to Γ point and the band gap becomes now direct with both VBM and CBM at the Γ point. As the pressure increases, however, there are still two important transition points for CBM shift in the band structure. One is CBM change from Γ point to **F** point occurring at 66.2 GPa, the other is CBM change from **F** point to **B** point occurring at 76.5 GPa.

Table 2. Under pressure, the VBM and CBM for high-symmetry BZ points in kaolinite.

Pressure/ GPa		High-symmetry				Pressure/ GPa		High-symmetry			
		Γ	B	F	G			Γ	B	F	G
0	CBM	6.871	9.228	9.167	7.781	66.2	CBM	14.614	14.759	14.614	15.522
	VBM	1.775	1.790	1.776	1.765		VBM	7.923	7.462	7.591	7.663
0.5	CBM	6.977	9.341	9.274	7.886	66.3	CBM	14.618	14.762	14.617	15.527
	VBM	1.863	1.864	1.854	1.854		VBM	7.925	7.465	7.593	7.665
0.6	CBM	7.007	9.368	9.301	7.914	70	CBM	14.853	14.880	14.767	15.743
	VBM	1.891	1.886	1.878	1.881		VBM	8.075	7.612	7.734	7.818
10	CBM	9.482	11.239	11.030	10.471	76.4	CBM	15.200	15.026	15.014	16.064
	VBM	4.131	3.904	4.002	3.680		VBM	8.264	7.835	7.889	7.997
20	CBM	11.179	12.705	12.377	12.290	76.5	CBM	15.212	15.021	15.028	16.075
	VBM	5.557	5.232	5.305	5.223		VBM	8.264	7.846	7.884	7.994
30	CBM	12.123	13.330	13.012	13.195	80	CBM	16.327	15.933	16.440	16.929
	VBM	6.215	5.877	5.958	5.930		VBM	8.232	7.633	7.740	8.201
40	CBM	12.920	13.824	13.522	13.942	90	CBM	16.669	16.383	16.579	17.158
	VBM	6.773	6.392	6.500	6.507		VBM	8.464	7.781	7.783	8.431
50	CBM	13.606	14.227	13.959	14.584	100	CBM	17.080	16.683	16.877	17.515
	VBM	7.252	6.828	6.963	6.994		VBM	8.767	8.068	8.041	8.723
60	CBM	14.262	14.571	14.387	15.194	110	CBM	17.451	16.966	17.162	17.851
	VBM	7.686	7.243	7.372	7.432		VBM	9.053	8.340	8.293	8.997

Fig. 3. (Color online) The energy of VBM and CBM as a function of the pressure for each high symmetric K point in kaolinite.

Fig. 4. (Color online) (a) and (b), respectively, represent the unit cell volume and band gap of kaolinite under pressure.

To obtain a more precise knowledge of pressure properties in kaolinite, furthermore, the volume (Fig. 4(a)) and values of E_g (Fig. 4(b)) under pressure are shown in Fig. 4, respectively. From Fig. 4(a), one can see that the volume of kaolinite exponentially decreases as the corresponding pressure increases from 0 GPa to 110 GPa, however, there is an obvious change in volume trend below 20 GPa. The main reason for this change is the distance between the kaolinite layers clearly reduced in the relative low-pressure range, whereas the chemical bond length shortened limitedly in the relative high-pressure range. Under pressure ranging from 0.6 GPa to 66.2 GPa, one can see from Fig. 4(b) that the corresponding band gap increases linearly with pressure and the pressure coefficient is 0.02425. With the increasing of pressure, direct band gap widened gradually from 5.08 eV ($p = 0$ GPa) to 6.69 eV ($p = 70$ GPa), which corresponds to an increase of the band gap by about 1.61 eV. As the pressure increases, the values of E_g have a sharp increase from 6.69 eV ($p = 70$ GPa) to 7.70 eV ($p = 80$ GPa) due to the transition from direct structure to indirect structure and this change is also illustrated in Fig. 3 for CBM shift in the band structure. Under high-pressure, the values of indirect band gap are stabilized when the pressure is greater than 80 GPa, which corresponds to the value of E_g which is around 7.92 eV.

The orbital-resolved site-projected density of states (PDOS) of Al, Si, O and H atoms in the kaolinite unit cell are shown in Fig. 5. It is found that, at $p = 0$ GPa, the sharp peak of the PDOS of O(interlayer), O(apical) and O(inner) is very near from the VBM, which means these O atoms have the main contribution in VBM. Under pressure, it is found that, the peak of total DOS split into two parts from

Fig. 5. (Color online) Orbital-resolved partial DOS for Si, Al, O and H atoms in kaolinite. (a), (b), (c), (d), (e) and (f), respectively, represent the stress value of 0 GPa, 20 GPa, 40 GPa, 60 GPa, 80 GPa and 100 GPa. The VBM is set at O eV.

20 GPa to 60 GPa in conduction band region, the peak of DOS moves toward high energy region from 80 GPa to 100 GPa and the DOS split phenomenon disappeared. As the pressure increases, we note that the PDOS shapes of Al, Si and four kinds of oxygen atoms remain similar, whereas there are some changes in PDOS of H atom. Specially, one can see that, the DOS peak height of H(interlayer) decreases from 0.07 ($p = 0$ GPa) to 0.04 ($p = 100$ GPa) in valence band region, which can result in the decreasing overlap of PDOS between H atom and O atom. The overlap phenomenon of PDOS between H atom and O atom is decreased with the increase of pressure, which also indicates that the bond strength of hydroxyl groups in kaolinite has been reduced.

4. Summary

In summary, the electronic structures and pressure properties of kaolinite were studied by using first-principles calculations. The calculated results show that, at $p = 0$ GPa, the VBM of the kaolinite is at the **B** point and the CBM is at the Γ point with the indirect band gap width of 5.08 eV. With the increasing of pressure, band gap widened from 5.08 eV ($p = 0$ GPa) to 7.92 eV ($p = 100$ GPa), which is mainly due to the shifting up of conduction band. At $p = 0.6$ GPa, band structure of kaolinite first converts an indirect gap into a direct gap, and then recovers an indirect gap structure at $p = 66.2$ GPa. Under pressure, bond strength of Al–O is weaker than that of the Si–O bond, and the bond strength of hydroxyl groups in kaolinite is reduced as pressure increases. It can be expected that the present first-principles results may be used to explain the various pressure behaviors of kaolinite from a microscopic viewpoint.

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