Surface Chemistry of Andalusite by Quantum Chemistry Calculation

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Abstract - The chemistry, reactivity sites and bond formation characteristics of andalusite surfaces were investigated by using quantum chemistry methods. The GGA-Pw91 exchange correlation functions and 410eV cut-off energy were used to analysis the crystal structure of andalusite from the respects of state density, Mulliken layout value, charge density and difference charge density. The results show that the band gap of andalusite is 5.025; the top of valence band is mainly composed of O(2p) orbit, and the bottom of conduction band is mainly composed of Al(sp) orbit, so the anionic collector mainly reacts with Al atoms while it adsorbs on the surface of andalusite; the ionicity of Al-O bond is stronger than Si-O bond, and when the mineral is crushed, mainly Al ions with unbalanced electrovalence exist on fracture surface, so it can be predicted that the broken dissociative surface of andalusite has strong hydrophilicity, which provides guidance for the selection of andalusite flotation reagents.

Keywords: andalusite; density functional theory; surface chemistry; quantum chemistry.

I. INTRODUCTION

With the development of iron and steel and ceramic industries, the importance of andalusite ore dressing is prominent increasingly. In addition to be used as high-quality refractory materials, andalusite also can be used for smelting high-strength lightweight silumin and manufacturing metal fiber and so on, and its application range is extending continuously. Andalusite ores usually contain 5−15% andalusite. Other minerals contained in the ores are mainly quartz, biotite and garnet . The ores must be beneficiated in order to be used for the refractory material industry. Many experimental research works have been done for the flotation theory of andalusite[1-3] all the time.

Along with the development of density functional theory and molecular force field method, quantum chemistry and molecular dynamics methods have made certain progress

in the field of mineral flotation. The quantitative calculation results for pyrite flotation have been reported [4-6] many times. As for andalusite, with the quantum chemistry methods of abinitio RHF (Hartree-Fock-Roothaan), and through calculating the interactional bond order and the adsorption heat of collectors sodium dodecyl sulfate and dodecylamine with andalusite respectively, Lingchu Zhou et al.[7] drew a conclusion that sodium dodecyl sulfate was chemical adsorption and dodecylamine is physical adsorption, and predicted that the collecting capacity of anionic collector sodium dodecyl sulfate on andalusite is larger than cationic collector dodecylamine, which is consistent with experimental results. In addition, there are some theory calculations [8-9] about andalusite, they mainly focus on its structure, bulk modulus and elastic constant, while the researches about relationship between crystal structure of andalusite bulk and flotation of andalusite are less.

In this paper, with the plane wave pseudo-potential method in density functional theory (DFT), the relationship between andalusite microstructure and its flotation performance was studied from the respects of states density, Mulliken population analysis, charge density and difference charge density. The calculation results provides basis for further study on the surface property of andalusite and its flotation performance.

II. CALAULATION MODEL AND METHOD

2.1 Caculation Model

Andalusite is nesosilicate mineral and belongs to orthorhombic system, whose chemical formula is Al_2SiO_5, structural formula is $AlO[AlSiO_4]$, theoretical chemical composition is Al_2O_3 63.1%, SiO_2 36.9%, space group is Pnnm, lattice constants of andalusite is a=7.7599Å,b=7.8735Å, c=5.544Å, α=β=γ=90°. In this paper, the model is an unit cell with 32 atoms that is one of

the andalusite crystal structures, which is shown in figure   1.
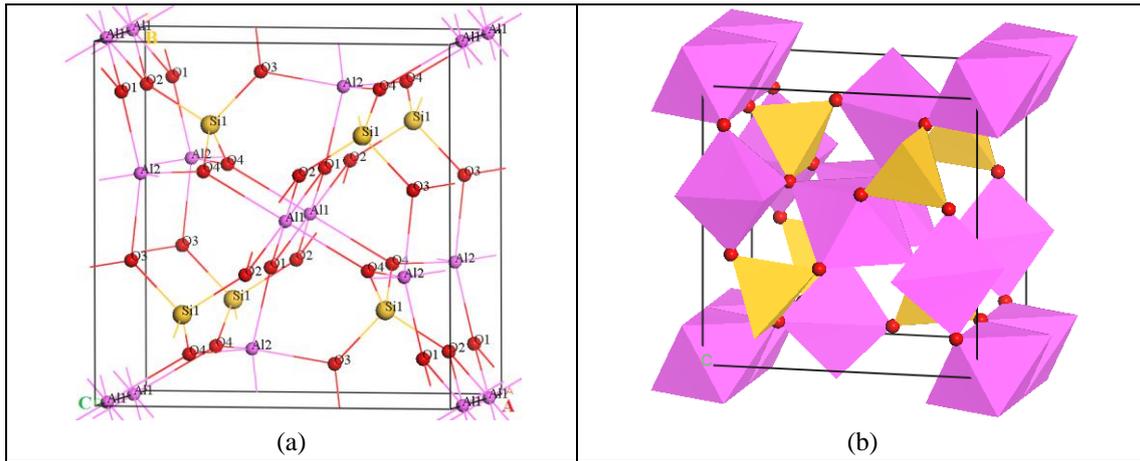
Figure .1   The (1×1×1) Unit Cell Structure Model of Andalusite: (a) Ball-and-Stick Model, (b) Polyhedral Model (notice: Al: ⬤, Si: ⬤, O: ⬤)

As known from figure 1, the coordinative tetrahedron [SiO$_4$] presents the state of isolated "islands" in the structure of andalusite, and half Al atoms form octahedron [AlO$_6$] in six-coordinated Al$_1$ and link in a chain along the c-axis, and the interchain is connected by trigonal bipyramid [AlO$_5$] formed by five-coordinated Al$_2$ and tetrahedron [SiO$_4$]. The atomic ratio of andalusite is Si : O > 1 : 4, because in tetrahedron the Si is connected with O$_2$, O$_3$ is connected with O$_4$, and O$_1$ is connected with Al$_1$ and Al$_2$, that is to say, the O in tetrahedron has two kinds of coordinations. The coordination of elements and types of bondings in andalusite[10] are shown in table 1.

Table 1 The Elements Coordination and Bonding Types in Andalusite

Coordination Conditions	Types of Metal-O bandings
Al$_1$ → 2O$_1$ + 2O$_2$ + 2O$_4$ Al$_2$ → O$_1$ + 2O$_3$ + 2O$_4$ Si → O$_2$ + O$_3$ + 2O$_4$ O$_1$ → 2Al$_1$ + Al$_2$ O$_2$ → 2Al$_1$ + Si O$_3$ → 2Al$_2$ + Si O$_4$ → Al$_1$ + Al$_2$ + Si	Al$_1$ — O$_1$ Al$_1$ — O$_2$ Al$_1$ — O$_4$ Al$_2$ — O$_1$ Al$_2$ — O$_3$ Al$_2$ — O$_4$ Si — O$_2$ Si — O$_3$ Si — O$_4$

2.2 Calculation Method

In this paper, the calculation is based on density functional theory. Firstly, the convergence test was carried on, which was in order to select suitable cut-off energy and the value of k. The result is shown in table 2 and table 3.

Table 2 The Convergence Test Results for Cut-off Energy (k: 3×3×5)

Cut-off Energy (eV)	System Energy (eV)	The Absolute Value of Energy difference Before and After (eV)
360	-9680.39495	---
370	-9680.52529	0.130
380	-9680.59310	0.066
390	-9680.62694	0.034
400	-9680.63630	0.009
410	-9680.64353	0.007
420	-9680.65110	0.008
430	-9680.66374	0.012

Table 3   The Convergence Test Results for K Value (Cut-off : 410eV)

Network of K-point	System Energy (eV)	The Absolute Value of Energy Difference Before and After (eV)
2×2×5	-9680.64388	---
3×3×5	-9680.64353	0.000346
4×4×5	-9680.75417	0.000053
5×5×5	-9680.64348	0.000007

As known from table 2, when the value of cut-off energy is 410eV, the difference between the calculated system energy value and two values before and after is respectively 7meV and 8meV, which is the minimum difference in this group, thus we could confirm the calculated cut-off energy was 410eV.

As known from table 3, with the increase of k-point sampling densities values, the system energy difference

before and after gradually decreases, and when the value of k-point is 4×4×5, the system has the lowest energy, which means that the system has been stable at the moment, so the 4×4×5 was selected as the value of k-point.

After confirming the selected cut-off energy and the k-point value, the four exchange-correlation functions (GGA-PW91, GGA-PBE, GGA-RPBE and LDA-CA-PZ) are compared so as to find the most stable bulk phase structure, the result is shown in table 4.

Table 4   The Comparison of Exchange-correlation Functions (Δ: The Relative Errors of Calculated Value and Experimental Value)

Cut-off Energy	The lattice constants (Å)			Energy (eV)
	a	b	c	
Experimental Value[10]	7.7599	7.8735	5.5440	
GGA-PW91	7.8359	7.9450	5.5891	-9678.24
Δ	0.98%	0.91%	0.81%	
GGA-PBE	7.8427	7.9528	5.5920	-9666.21
Δ	1.07%	1.01%	0.87%	
GGA-RPBE	7.8816	7.9811	5.5946	-9673.98
Δ	1.57%	1.37%	0.91%	
LDA-CA-PZ	7.6442	7.7676	5.4695	-9679.97
Δ	-1.49%	-1.35%	-1.34%	

As known from table 4, after that using GGA-PW91 to geometrically optimize the calculation model, we got the calculated value of the lattice constant that is consistent with the experimental value[11], and the error is less than 1%, which is in the typical error range of 0~2%. That is because the value with pseudopotential plane wave method is different from the value with experiment method. In addition, our calculated temperature is 0 k, while the experimental value is measured under the condition of 298 k, and the lattice constant of andalusite is changed with temperature[12], so the error may be caused by temperature. Therefore, our calculated results are reliable, and the GGA -PW91 is used as exchange-correlation functions in the following calculation.

III. RESULTS AND DISCUSSION

3.1 The Structural Parameters

Firstly, the calculated model was geometrically optimized so as to adjust the lattice parameters and the atomic position to make total energy of system lowest and get the most stable structure. Table 5 shows the the comparative results about the calculated values and experimental values[11] of atomic fraction coordinates in andalusite.

Table 5   The Calculated Values and Experimental Values of Atomic Fraction Coordinates in Andalusite

		x	y	z
Al1	Calculated Values	0.0000	0.0000	0.2417
	Experimental Values	0.0000	0.0000	0.2416
Al2	Calculated Values	0.3705	0.1391	0.5000
	Experimental Values	0.3702	0.1391	0.5000
Si	Calculated Values	0.2459	0.2523	0.0000
	Experimental Values	0.2459	0.2514	0.0000
O1	Calculated Values	0.4235	0.3629	0.5000
	Experimental Values	0.4221	0.3634	0.5000
O2	Calculated Values	0.4240	0.3631	0.0000
	Experimental Values	0.4249	0.3623	0.0000
O3	Calculated Values	0.1030	0.4001	0.0000
	Experimental Values	0.1031	0.4000	0.0000
O4	Calculated Values	0.2313	0.1346	0.2389
	Experimental Values	0.2303	0.1327	0.2389

As known from table 5, the calculated model and

experimental model have good consistency, which shows that the geometrically optimized structure is stable and reliable and can be used to calculate the correlation properties of andalusite.

3.2 The Result Analysis of Band Structure and Density of States

Based on the geometry optimization of andalusite crystals, the band structure and the corresponding density of states are obtained and shown in figure 2. The Fermi level E_F was located at 0 eV., only the band structure and density of states which is near to the Fermi level was made in figure 2, and the value of scissors was 0 eV.
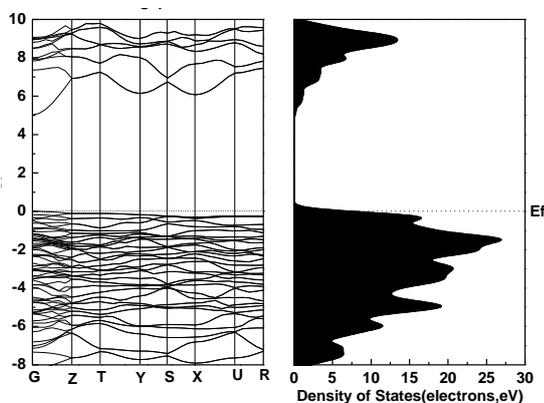
Figure. 2 Energy-Band Structure (Left) and Density of States (Right) for Andalusite   Crystal.

As known from figure 2, the andalusite crystals have direct band gap whose value is 5.025eV. And the energy band fluctuation is large, which means the effective mass of electron in the band is small, the degree of non-local area is high and the atomic orbits forming the band have strong extensibility. Besides, the bandwidth of the energy band depends on the bonding strength in periodic direction of atomic orbits. The stronger the intensity is, the larger the bandwidth is, on the contrary, the weaker the bonding is, the smaller the bandwidth is. Density of states and ennergy band structure are corresponding. As shown in figure 2, the denser the band is, the greater the density of states is; the more flat the band is, the shaper the peak of density states is; the wider the band is, the smoother the density of states is; and the stronger the delocalization is, the stronger the bonding is, which are consistent with the analysis of the band. In this paper, the calculated value of band gap(5.025eV) has good consistency with Cano and Watanabe's[13] value (5.01 eV) taht is calculated by the

Full-potential Linearized Augmented Plane-Wave method (FP - LAPW) of density functional theory, which shows that our theoretical calculation is credible.

In order to further analyze the interaction of the atoms in andalusite, the total density of states and the partial density of states of each atom were made, and two types of Al atoms and four types of O atoms were made respectively. The Fermi level E_F was still located at 0eV. The valence electron orbit of each atom in andalusite was selected as follows: Al: 3s3p, Si: 3s3p, O: 2s2p. The results are shown in figure 3.
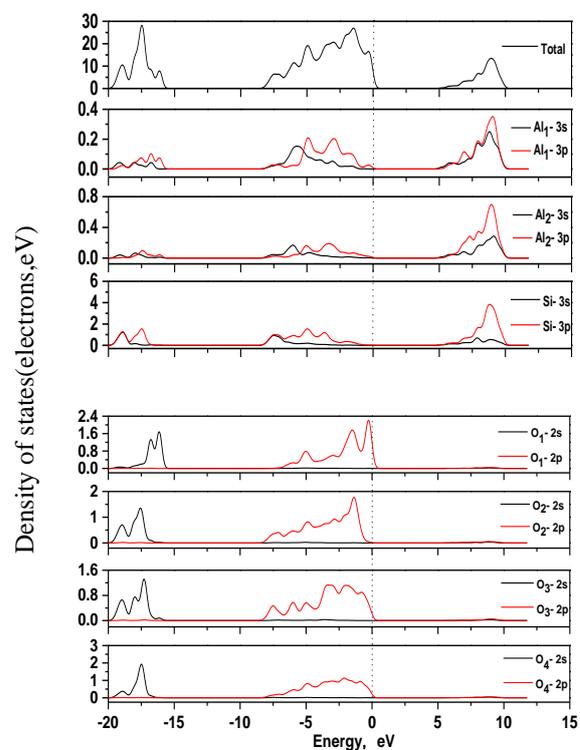
Figure .3   The States Density of Andalusite

As known in figure 3, the lower valence band (lower-VB) is mainly composed of O(2s) orbits, and the upper valence band (upper-VB) is composed of O(2p), Al(3s), Al(3p), Si(3s) and Si(3p), which shows that the bondings exist between the O atoms with Al and Si, and the states density of Si appear at the lower energies compared with the states density of Al, and the s-p orbit is separate obviously. The high-energy region of valence band between -2 and 0eV is mainly composed of O(2p) orbits with little orbits of Si and Al, while the energy region of valence band near -5 eV is mainly composed of the orbits of Si, Al and O(2p). The upper-VB width is

about 8 eV, and parts of O(2p) orbits near Fermi level are across the Fermi level, and the literature[14] points out that this phenomenon shows the ionicity of materials is enhanced. The conduction band (CB) is mainly composed of s-p orbits of Si and Al. The nuclear electric charges of O atoms and Al atoms in different positions participate in bonding with different levels. The valence-band maximum of andalusite is mainly composed of O(2p) orbits, while the bottom of the conduction band is mainly composed of Al(sp) orbits. When the anionic collector adsorbs the minerals on the surface of andalusite, it may react with the Al atoms on the surface, which is consistent with the functional mechanism of anions like sodium dodecyl sulfate.

3.3 Mulliken Population Analysis

The influence of density of states on bonding strength is difficult to be explained quantitatively. In view of that, we analyzed the population analysis. The Mulliken population analysis contains atomic population analysis and bond population analysis. Except for O_4, there are two locations of other atoms, and in order to distinguish them, the atoms inside the cell are marked by the subscript f. The Mulliken population values of atoms and bonds in andalusite crystals are shown in table 6 and table 7 respectively.

Before the optimization, the valence electron configurations of andalusite are as follows: $Al(3s^2 3p^1)$, $Si(3s^2 3p^2)$, $O(2s^2 2p^4)$. As known from $Al_1(3s^{0.48}3p^{0.81})$, $Al_2(3s^{0.44}3p^{0.68})$, $Si(3s^{0.66}3p^{1.24})$, $O_1(2s^{1.85}2p^{5.31})$, $O_2(2s^{1.84}2p^{5.29})$, $O_3(2s^{1.85}2p^{5.31})$, $O_4(2s^{1.85}2p^{7.13})$ in table 6 after the optimization, the same kind of atom's charge distribution is different in different positions. The electron numbers localized on the O atoms are 7.16, 7.12 and 7.13 respectively, which are the electron acceptors, and the electrons obtained correspondingly are 1.16, 1.12 and 1.13 with charges of -1.16, -1.12 and -1.13 respectively, which are mainly obtained by 2p orbit; the electron numbers localized on the Al atoms are 1.29 and 1.11 respectively, which are the electron donors, and the electrons loss correspondingly are 1.71 and 1.89 with charges of 1.71 and 1.89 respectively, which are mainly loss from the S orbit; the electron numbers localized on the Si atoms are 1.90, which are the electron donors, and the electrons loss correspondingly is 2.10 with charges of 2.10, which are

mainly lose from the S orbit.

Table 6   Mulliken Population Values of Atoms

Mineral	Species	s	p	Total	Charge
Andalusite	Al1	0.48	0.81	1.29	1.71
	Al2	0.44	0.68	1.11	1.89
	Si	0.66	1.24	1.90	2.10
	O1	1.85	5.31	7.16	-1.16
	O2	1.84	5.29	7.12	-1.12
	O3	1.85	5.31	7.16	-1.16
	O4	1.85	5.28	7.13	-1.13

Table 7   Mulliken Population Values of Bonds

Mineral	Bond	Population	Length/Å
Andalusite	$Al_1 - O_1$	0.39	1.836
	$Al_1 - O_2$	0.33	1.903
	$Al_1 - O_4$	0.25	2.104
	$Al_2 - O_1$	0.40	1.826
	$Al_2 - O_3$	0.28	1.910
	$Al_{2f} - O_{3f}$	0.32	1.848
	$Al_2 - O_4$	0.37	1.823
	$Si - O_2$	0.56	1.649
	$Si - O_3$	0.54	1.623
	$Si - O_4$	0.59	1.634

As known from table 7, the octahedron in andalusite has distortion: the bond length of four O atoms (two O_1 and two O_2) bonding with Al_1 in the same plane are 1.836 Å and 1.903 Å respectively, while the bond length of two O_4 atoms located in further point bonding with Al_1 are 2.104Å (0K); O_1, O_{3f}, O_4 and O_4 located in the top of pyramid form a triangle pyramid, and the bond length of O_1-Al_2, O_{3f}-Al_2, O_4-Al_2, Al_2-O_3 is 1.826 Å, 1.848 Å, 1.823 Å and 1.910 Å respectively, and then O_1, O_{3f} and O_4 bonding with O_3, which forms a complete bipyramid, and the bond length of Al_2-O_3 is 1.910Å. The maximum value of Al-O population is 0.40, while the minimum value of Si-O population is 0.54, which shows that Si-O bands present a strong covalency[15]. According to auling's empirical formula[10], (1) the ionicity of compounds was calculated, in which the electronegativity values of Si, O and Al respectively are: 1.90, 3.44, 1.61[16].

$$\varphi = 100[1 - \exp^{\frac{-(x_A - x_B)^2}{4}}] \qquad (1)$$

In formule, φ is the percentage of ionic bond in compound, x_A and x_B are the electronegativity of atoms in compounds.

The ionic bond percentage of Si-O and Al-O calculated from the formula is respectively 44.73% and 56.71%, which are consistent with the calculation results. In the mineral structure, the higher the ingredient of ionic bond in atoms is, the greater the polarity of bonds is, and the easier the band is to break[10]. This calculation result theoretically shows that mainly Al ions with unbalanced electrovalence exist on fracture surface of andalusite, and the content of Si ions is relatively not high. The broken dissociation surface has more Al^{3+}, and we can predict that there is strong hydrophilicity on the broken dissociative surface of andalusite.

3.4 Electric Charge Density and Deformation Charge Density

In order to further understand the atomic bonding in andalusite and its electronic structure, we investigated the electric charge density and deformation charge density at the center of AB surface in andalusite, the result is shown in figure 4(a) and (b).
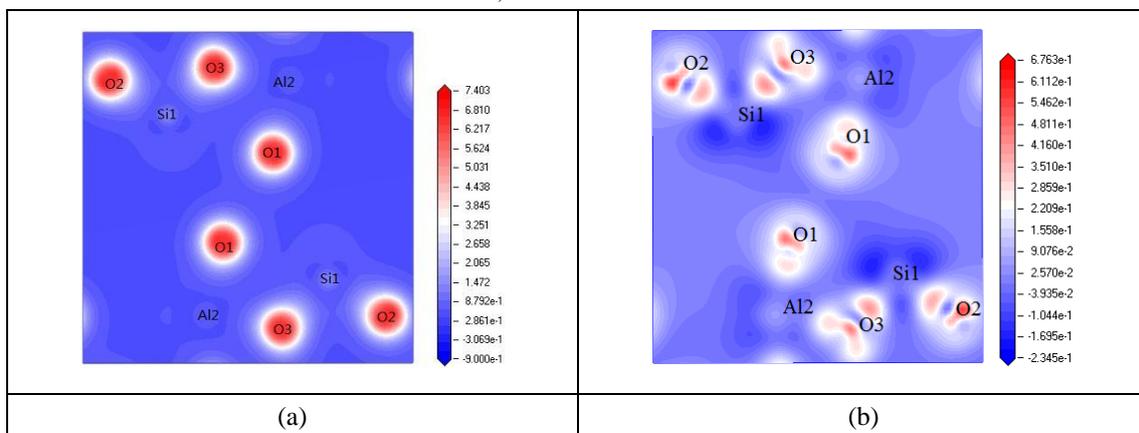
Figure 4 Electric Charge Density (a) and Deformation Charge Density (b)

As known from figure 4(a), the electron cloud overlap between Al and O atoms is obviously smaller than the electron cloud overlap between Si and O atoms, which indicates the ionicity of Al-O atoms is stronger than the ionicity of Si-O atoms. Looking from charge distribution, the electron cloud mainly concentrates near the O atom, so the electron slants to O atom and makes it get electrons and have negative electricity, on the contrary, Al and Si lose electrons and have positive electricity. The analysis results are consistent with the analysis results of Mulliken population values. The deformation charge density in figure (b) shows that there is strong charge transfer between Si and O atoms, and that indicates the it forms strong direction covalent bonds between two atoms. The stronger the band covalency is, the greater the polarization force to water molecules is, and natural flotability of mineral becomes worse. Therefore, polarity collectors will be used when floating covalent minerals. And ionic bond can make mineral surface form thick hydrated film, and make minerals hydrophilicity become stronger, which prevents the effect of agentia and mineral, and then affects its floatability.

IV. CONCLUSION

(1) When the k-point value is taken as 4×4×5 and the cut-off energy is taken as 410eV, the system reaches convergence, on this basis, when exchange-correlation function is taken as GGA-PW91, we get the bulk phase with the most stable energy.

(2) The analysis result of states density shows that there is hybridization among O(2p), Al(sp) and Si(sp) orbits in upper valence band, and there is charge transfer between O atom with Al atom and Si atom; when the anionic collector adsorbs on the mineral surface of andalusite, it will firstly interact with Al atoms on the surface, and when cationic collector adsorbs on the mineral surface of andalusite, it will firstly interact with O atoms on the surface.

(3) Mulliken population analysis, electric charge density and deformation charge density all show that the ionocity of Al-O band is stronger than the ionocity of Si-O band,

and there are many Al^{3+} on the broken dissociative surface.

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