Article

Study of the Effect of Absorbed Cu Species on the Surface of Specularite (0 0 1) by the DFT Calculations

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Abstract: Cu²⁺ exhibited a good activation effect on specularite. However, its microscopic activation mechanism needs further study. Additionally, Cu²⁺ was mainly present in the flotation solution as Cu²⁺, Cu(OH)⁺, and Cu(OH)₂ at pH = 7. Therefore, density functional theory (DFT) calculations were used to investigate the effect of Cu species such as Cu²⁺, Cu(OH)⁺, and Cu(OH)₂ adsorbed on the crystal structure and properties of the specularite (0 0 1) surface. The adsorption mechanism of different Cu components on the surface was also further clarified by the analyses of the adsorption model, adsorption energy, partial density of states (PDOS), charge transfer, and bond properties. In addition, the obtained results are discussed. Based on the obtained results, it can be concluded that the geometric structure and electronic properties on the surface changed after adsorbing Cu components and that the O3–Fe1–O1 structure was more susceptible to the adsorbates. The adsorption engines results show that Cu components could be spontaneously adsorbed onto the specularite (0 0 1) surface with adsorption energies of −0.76, −0.85, and −1.78 eV, corresponding to Cu²⁺, CuOH⁺, and Cu(OH)₂, respectively. Therefore, the adsorption stability of the Cu species on the specularite surface increased in the order of Cu²⁺ < Cu(OH)⁺ < Cu(OH)₂. Additionally, the adsorption sites for Cu species on the surface were different. Cu²⁺ interacted mainly with O atoms on the surface, forming Cu–O complexes, while Cu(OH)⁺ and Cu(OH)₂ acted mainly through the O atom of –OH, interacting with Fe atoms to form Cu–O–Fe complexes. The formation of Cu–O and Cu–O–Fe complexes increased the adsorption sites for sodium oleate, with more hydrophobic species being generated to improve the floatability of specularite.

Keywords: specularite; Cu species; crystal structure and properties; activation mechanism; DFT

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1. Introduction

Copper ions are often used as an activating ion in flotation to increase the floatability of minerals, and there were many studies on the activation mechanisms of copper ions on metallic sulfide minerals (e.g., sphalerite and pyrite) and nonmetallic oxidized ore (e.g., chlorite and quartz) [1–3]. Scholars [4,5] analyzed the hydrolysis products of Cu²⁺ in different pH ranges by solution chemistry calculations. Cu²⁺ could be hydrolyzed in the aqueous solution with the change of pH to form five components: Cu²⁺, Cu(OH)⁺, Cu(OH)₂, Cu(OH)₃[−], and Cu(OH)₄^{2−}. At pH less than 7.0, Cu²⁺ was the predominant species, and CuOH⁺ and Cu(OH)₂ became the main species at pH of 7.0–10.7, while at pH greater than 10.7, the copper species in the solution were mainly in the form of Cu(OH)₂, Cu(OH)₃[−], and Cu(OH)₄^{2−}.

Flotation is one of the most common methods used to recover iron ore, which includes reverse flotation of gangue with cationic collector [6–8] and direct flotation of iron ore with anionic collector [9–11]. Compared with reverse flotation, direct flotation of iron ore

has the advantages of being a simple process and having convenient operation and low production cost. Therefore, studying the direct flotation of iron ore is of great significance to the comprehensive utilization of iron resources. However, the flotation index of specularite is relatively poor. Thus, efficient recovery of specularite is crucial to the comprehensive utilization of iron ore.

A previous study [12] showed that Cu^{2+} had a good activation effect on specularite. When the concentration of Cu^{2+} was 63.55 mg/L, the concentration of NaOL was 1.5 mg/L, the pH was 7, and the recovery of specularite reached 74.63%. The activation mechanism of Cu^{2+} on specularite with sodium oleate as the collector was investigated via zeta potential measurement and solution chemistry calculation. The results of zeta potential measurement showed that the adsorption of Cu species could positively shift the surface potential to promote the adsorption capacity of sodium oleate on a specularite surface. The results of solution chemistry calculation showed that Cu^{2+} was mainly present in the flotation pulp as Cu^{2+} , $\text{Cu}(\text{OH})^+$, and $\text{Cu}(\text{OH})_2$ at a pH = 7. However, the previous studies did not comprehensively discuss the influence of Cu^{2+} adsorption on the crystal structure and properties of specularite or its activation mechanism. It is difficult to elaborate the microscopic mechanism of Cu^{2+} activation of specularite using only experimental methods.

Density functional theory (DFT) is a method for studying the electronic structure of multi-electron systems [13], and it is widely used in flotation processes [14–17]. It can be used to investigate the mechanism of the interaction between the agents and the minerals surface during flotation. Zhao et al. [18] verified that cyclohexyl isohydroxamic acid (CHA) was better than benzhydroxamic acid (BHA) as a flotation collector for scheelite using DFT calculations. Li et al. [19] used the DFT calculations to investigate the structure-activity of chelating collectors for flotation. DFT calculations can also be used for the influencing mechanism of activators, inhibitors, and dispersants on the target minerals in flotation systems. Zhao et al. [20] used the DFT calculations to investigate the effect of different adsorption sites of HS^- on the smithsonite (1 0 1) surface on the surface structure and properties and revealed the optimal adsorption sites of HS^- on the smithsonite surface. Liu et al. [21,22] explored the mechanism of Cu adsorption on the sphalerite (1 1 0) surface by DFT calculations. Deng et al. [3,23] used the DFT/B3LYP method to simulate the interaction between ethyl xanthate and Cu/Fe ions and calculated the action mechanism of Cu^{2+} on chalcopyrite surface using DFT. Lin et al. [24] used the DFT calculations to investigate the inhibition behaviors and mechanism of bismuthinite flotation by pyrogallol. Han et al. [25] used DFT calculations to study the crystal structure and surface properties of clay minerals, such as kaolin and smectite, which have a serious impact on the flotation process from a microscopic point of view, and their interactions with commonly used dispersants and inhibitors mechanism were studied. The above results indicate that DFT calculations are applicable to various applications of surface science, and they can complement the action mechanism of agents and mineral surfaces. Therefore, it is reasonable to use DFT calculations to simulate the mechanism of action of Cu species on the surface of specularite.

The current study used DFT simulation to construct adsorption models of Cu^{2+} , $\text{Cu}(\text{OH})^+$, and $\text{Cu}(\text{OH})_2$ on a specularite (0 0 1) surface and to optimize the structures, as well as to explore the influence of Cu species on the crystal structure and properties of specularite (0 0 1) surface. Additionally, the adsorption mechanism of Cu species on the surface of specularite was studied by an adsorption model, adsorption energy, partial density of states (PDOS), charge transfer, and bond properties, etc. The microscopic activation mechanism of Cu^{2+} absorbed on specularite is illustrated at atomic scale.

2. Computational Details

DFT calculations were accomplished using the CASTEP module in Material Studio 2017 software. The exchange correlation functional adopted the Perdew–Wang 91 (PW91) gradient correction under the generalized gradient approximation (GGA) and used the BFGS algorithm to optimize the structure of the model [26]. The cutoff energy was 400 eV.

The convergence tolerances were set as follows: energy tolerance, 2×10^{-5} eV/atom; maximum force tolerance, 0.05 eV/Å; maximum displacement tolerance, 0.002 Å; maximum stress, 0.1 GPa; SCF tolerance, 1×10^{-6} eV/atom. If there was no special explanation, all parameter settings were consistent during the calculation process.

First, the original unit cell of specularite was constructed. The unit cell parameters were $a = b = 5.03$ Å, $c = 13.75$ Å, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$. Li et al. [27] studied the surface energy of several specularite crystal surfaces through DFT calculations, and the results showed that the (0 0 1) surface of specularite has the lowest surface energy. Therefore, the (0 0 1) surface was constructed according to the overall structure of specularite. A $2 \times 2 \times 1$ supercell with 12 atomic layers was used for the simulation. The vacuum-layer thickness was set to 40 Å to avoid the interaction between the surface structure layers as well as to eliminate the effect of periodicity. The optimal surface structure was obtained by optimizing the geometry of the supercell, as shown in Figure 1. Then, the optimized Cu species were placed on the surface of the model, and their interaction was simulated.

Figure 1. Specularite Fe_2O_3 (0 0 1) surface: (a) front view, (b) vertical view.

The stability of adsorbates surface could be determined using the adsorption energies (E_{ads}) [25], and the adsorption energy of the adsorbates on the specularite surface was calculated as follows [28–30]:

$$E_{\text{ads}} = E_{\text{adsorbate/slab}} - (E_{\text{adsorbate}} + E_{\text{slab}}) \quad (1)$$

where E_{ads} represents the adsorption energy; $E_{\text{adsorbate/slab}}$ represents the energy of the adsorbed specularite (0 0 1) surface; $E_{\text{adsorbate}}$ represents the energy of the adsorbate; and E_{slab} represents the energy of the specularite (0 0 1) surface. The more negative the adsorption energy, the stronger the interaction between the adsorbates and the specularite surface [31,32].

3. Results and Discussion

3.1. The Effect of Cu Species Adsorbed on the Structure of the Specularite (0 0 1) Surface

Copper ions were hydrolyzed into different species in an aqueous solution as a function of pH. Previous studies [12] had shown that specularite modified with Cu^{2+} has better floatability. In addition, Cu^{2+} , $\text{Cu}(\text{OH})^+$, and $\text{Cu}(\text{OH})_2$ were the main species of copper ions in flotation pulp under $\text{pH} = 7$. Therefore, the adsorption models of three

Cu components on the specularite (0 0 1) surface were constructed and optimized by DFT calculations to comprehensively understand the adsorbing detail of Cu components. Figure 2 lists the adsorbed specularite models of different Cu components before and after optimization. The migration of atoms can be found on specularite (0 0 1) surface after geometrical optimization.

Figure 2. Cont.

Figure 2. The specularite (0 0 1) surface models with original and various Cu species adsorption before and after optimization: (a) original, (b) Cu^{2+} , (c) $\text{Cu}(\text{OH})^+$, (d) $\text{Cu}(\text{OH})_2$.

Differences in the geometric structure of the specularite (0 0 1) surface modified with Cu species can be concluded. The respective bond lengths of some atoms on the specularite (0 0 1) surface are shown in Table 1. The bond lengths of Fe–O on specularite (0 0 1) surface untreated with Cu species were 1.749 Å, 1.918 Å, 1.910 Å, and 1.749 Å after optimization. When Cu^{2+} adsorbed on the specularite (0 0 1) surface, the bond lengths of Fe–O were 1.809 Å, 1.943 Å, 1.925 Å, and 1.764 Å. When $\text{Cu}(\text{OH})^+$ adsorbed on the specularite (0 0 1) surface, the bond length of Fe–O on specularite (0 0 1) surface became 1.887 Å, 1.912 Å, 1.926 Å, and 1.775 Å. Additionally, when $\text{Cu}(\text{OH})_2$ adsorbed on the specularite (0 0 1) surface, the bond lengths of Fe–O on the specularite (0 0 1) surface were 1.844 Å, 1.908 Å, 1.930 Å, and 1.722 Å, which indicates that obvious variation occurs on the bond lengths of Fe and O on specularite (0 0 1) surface after Cu species adsorption. In other words, the variation of Fe–O near adsorbates surface is more favorable, and the bond lengths change differently when Cu components adsorbed on the specularite (0 0 1) surface.

Table 1. Neighboring bond length before and after Cu species adsorption on specularite (0 0 1) surface.

Adsorbates	Bond Length (Å)			
	Fe1–O1	O1–Fe2	Fe2–O2	O3–Fe1
Original	1.749	1.918	1.910	1.749
Cu^{2+}	1.809	1.943	1.925	1.764
$\text{Cu}(\text{OH})^+$	1.887	1.912	1.926	1.775
$\text{Cu}(\text{OH})_2$	1.844	1.908	1.930	1.722

The differences of bond angles on specularite (0 0 1) surface could be found after Cu species adsorption. Table 2 shows the bond angles of Fe and O on specularite (0 0 1) surface after various Cu species adsorption. The bond angles of Fe1–O1–Fe2, O1–Fe2–O2, O3–Fe1–O1, O1–Fe2–O4, and O4–Fe2–O2 on the untreated specularite surface were 118.461°, 101.402°, 115.903°, 86.237°, and 82.717°, respectively. After adsorption with Cu^{2+} component, the bond angles of these were turned to 119.474°, 100.695°, 108.848°, 87.559°, and 83.609°, respectively. In comparison, the bond angles of Fe1–O1–Fe2, O1–Fe2–O4, and O4–Fe2–O2 increased by 1.013°, 1.322°, and 0.892°, respectively; the bond angles of O1–Fe2–O2 and O3–Fe1–O1 decreased by 0.707° and 7.055°, respectively. When $\text{Cu}(\text{OH})^+$ adsorbed on specularite (0 0 1) surface, the bond angles of Fe1–O1–Fe2, O1–Fe2–O2, O3–Fe1–O1, O1–Fe2–O4, and O4–Fe2–O2 were changed to 119.829°, 99.038°, 111.672°, 86.879°, and 83.956°, respectively. In comparison, the bond angles of Fe1–O1–Fe2, O1–Fe2–O4, and O4–Fe2–O2 increased by 1.368°, 0.642°, and 1.239°, respectively; those of O1–Fe2–O2, and O3–Fe1–O1 decreased by 2.364° and 4.231°, respectively. After $\text{Cu}(\text{OH})_2$ adsorbed on the surface, the

bond angles of Fe1–O1–Fe2, O1–Fe2–O2, O3–Fe1–O1, O1–Fe2–O4, and O4–Fe2–O2 became 118.235°, 100.270°, 112.594°, 87.574°, and 83.873°. In comparison, the bond angles of O1–Fe2–O4 and O4–Fe2–O2 increased by 1.337° and 1.156°, respectively; those of Fe1–O1–Fe2, O1–Fe2–O2, and O3–Fe1–O1 decreased by 0.226°, 1.132°, and 3.309°, respectively. The results indicate that the structure of O–Fe–O and Fe–O–Fe on the specularite surface was influenced by the Cu species adsorbed. When Cu species adsorbed on specularite (0 0 1) surface, the variation of bond angle of O3–Fe1–O1 was maximum, indicating that the O3–Fe1–O1 near the Cu components on the specularite surface was more influenced by Cu species absorbed.

Table 2. Neighboring bond angles before and after Cu species adsorption on specularite (0 0 1) surface.

Adsorbates	Bond Angles (°)				
	Fe1–O1–Fe2	O1–Fe2–O2	O3–Fe1–O1	O1–Fe2–O4	O4–Fe2–O2
Original	118.461	101.402	115.903	86.237	82.717
Cu ²⁺	119.474	100.695	108.848	87.559	83.609
Cu(OH) ⁺	119.829	99.038	111.672	86.879	83.956
Cu(OH) ₂	118.235	100.270	112.594	87.574	83.873

3.2. The Effect of Cu Species Adsorption on the Electronic Properties of Specularite

To understand the effect of Cu²⁺ adsorption on the surface electronic properties of specularite, the PDOS of the Fe and O atoms on original and Cu-modified specularite surface were analyzed. The results show that the PDOS of surface atoms changed after Cu species adsorbed on the specularite (0 0 1) surface. Figure 3 shows the PDOS of Fe1 atom on specularite (0 0 1) surface before and after treatment with Cu²⁺. The black dotted line at 0 eV in the figure represents the Fermi level. The valence electron configuration of the Fe atom was Fe 3d⁶ 4s². The PDOS of Fe atom was composed of 4s, 3p, and 3d orbitals, and the PDOS of Fermi level was mainly contributed by the Fe 3d orbital. Compared with the results before Cu²⁺ adsorption (Figure 3a), the PDOS of Fe atom changed significantly after Cu components adsorbed on the surface of the specularite. After Cu²⁺ component adsorbed on the specularite surface (Figure 3b), the PDOS of Fe 3d orbital on the surface decreased, and a new Fe 3d orbital peak appeared at about −2 eV, while the PDOS of Fe 3p orbital decreased. After Cu(OH)⁺ adsorbed on the specularite surface (Figure 3c), the peak of Fe 3d orbital increased strongly. Similarly, the number of Fe 3d orbital peaks also increased to a certain extent. However, the PDOS peak of Fe 3d orbital disappeared after 4 eV. Although the PDOS peak of Fe 4s orbital increased, its peak near the Fermi level disappeared, which indicates that the contribution of Fe 4s orbital to Fe atom activity was reduced. It is noteworthy that the two new PDOS peaks of the Fe 4s orbital and a new PDOS peak of the Fe 3d orbital appeared at around −20 eV. This may have been caused by the interaction between the Fe atom on the surface of specularite and the Cu(OH)⁺ component. After Cu(OH)₂ adsorbed on the surface of specularite (Figure 3d), the PDOS of the Fe 3d orbital disappeared after 4 eV. The PDOS of the 4s orbital increased, but its PDOS peak near the Fermi level disappeared, indicating that the contribution of the 4s orbital to the activity of Fe atoms decreased. It is worth noting that the PDOS of Fe 4s and Fe 3d orbitals each added a new peak at around −20 eV, which may have been caused by the interaction of the Fe atom on the surface of the specularite and Cu(OH)₂ component.

The adsorption of Cu species on the surface of specularite can also cause changes in the PDOS of O atoms. Therefore, the changes in the PDOS of O atom on the surface before and after the adsorption of Cu components on the specularite surface were studied (Figure 4). The valence electron configuration of O was 2s² 2p⁴, which indicates that the PDOS of the O atom was composed of 2s and 2p orbitals. As shown in Figure 4, the PDOS of O 2s orbital made little contribution to the reactivity of the O atom on the surface that was far from the Fermi level, and the PDOS vicinity of the Fermi level was mainly contributed

by the O 2p orbital. Compared with the PDOS before the Cu components adsorbed, the position of the O atom PDOS peak did not move significantly, but the peak intensity had a certain change. In particular, the PDOS of the O atom changed most obviously after the Cu^{2+} component adsorbed on the specularite (0 0 1) surface. After Cu^{2+} adsorbed on the surface of the specularite (Figure 4b), the PDOS peak intensity of the O 2s orbital on the surface was significantly reduced, and the PDOS peak intensity of O 2p orbital was significantly enhanced, especially the PDOS peak at -2 eV. After $\text{Cu}(\text{OH})^+$ and $\text{Cu}(\text{OH})_2$ adsorbed on the specularite surface (Figure 4c,d), the PDOS of the O 2s orbital and the O 2p orbital changed little. These indicate that there was a strong interaction between the O atoms on the surface of the specularite and the Cu^{2+} component, but its adsorption of $\text{Cu}(\text{OH})^+$ and $\text{Cu}(\text{OH})_2$ showed weak reactivity.

Figure 3. PDOS of Fe1 atom on the surface of different adsorption models. (a) Initial configuration, (b) after Cu^{2+} adsorption, (c) after $\text{Cu}(\text{OH})^+$ adsorption, and (d) after $\text{Cu}(\text{OH})_2$ adsorption.

3.3. Adsorption of Cu Species on the Surface of Specularite

3.3.1. The Role of Cu Species Absorbed on the Surface of Specularite

Figure 2 shows the adsorption model of different Cu components on the specularite (0 0 1) surface before and after geometric optimization. The distance between the atoms in the adsorbate and that of the surface before and after the optimization and the adsorption energy (E_{ads}) of the different Cu components are listed in Table 3.

Figure 4. PDOS of O1 atom on the surface of different adsorption models. (a) Initial configuration, (b) after Cu^{2+} adsorption, (c) after Cu(OH)^+ adsorption, and (d) After Cu(OH)_2 adsorption.

Table 3. Interaction distance and adsorption energy of Cu species before and after adsorption on the surface of specularite.

Adsorbates		$D_{\text{Cu-Fe1}}$ (Å)	$D_{\text{Cu-O1}}$ (Å)	$D_{\text{Fe1-O1}}$ (Å)	$D_{\text{Fe2-O1}}$ (Å)	Energy (eV)
Cu^{2+}	Before	1.614	1.613	—	—	—
	After	2.387	1.987	—	—	−0.76
CuOH^+	Before	1.665	1.661	1.538	—	—
	After	2.808	1.985	1.854	—	−0.85
Cu(OH)_2	Before	1.708	1.713	1.721	2.296	—
	After	2.750	2.146	1.887	1.909	−1.78

When Cu^{2+} was placed on the (0 0 1) surface of the specularite (as shown in Figure 2b), the distances between the Cu atoms and Fe1 and O1 atoms on the specularite surface were 1.614 Å and 1.613 Å, respectively. After geometric optimization, the distance between Cu and O1 atoms on the surface increased to 1.987 Å, but it was smaller than the sum of the radii of Cu and O atoms. When the distance between two atoms was close to or less than the sum of their atomic radii, a chemical bond was formed between these atoms [33,34], indicating that Cu atoms and O1 atoms on the surface may form Cu–O

chemical bonds. Among them, the distance between Cu and Fe1 atoms increased to 2.387 Å, which was larger than the distance between Cu and O1 atoms, indicating that the O atoms on the surface of specularite (0 0 1) had a stronger adsorption effect on Cu^{2+} and that the adsorption of Cu^{2+} on the specularite surface was mainly through Cu atom bonding with O1 atoms on the surface. The adsorption energy of Cu^{2+} on the surface of specularite was calculated to be -0.76 eV, and a negative value indicates that the adsorption of Cu^{2+} component on the (0 0 1) surface of specularite was spontaneous.

When $\text{Cu}(\text{OH})^+$ was placed on the specularite (0 0 1) surface (as shown in Figure 2c), the distances between the Cu atoms of $\text{Cu}(\text{OH})^+$ and the Fe1 and O1 atoms on the specularite surface were 1.665 Å and 1.661 Å, respectively, and the distance between O1 atom of $\text{Cu}(\text{OH})^+$ and Fe1 atoms on the specularite surface was 1.538 Å. After geometric optimization, the bond length between the Cu atom and the surface O1 atom increased to 1.930 Å, but it was less than the sum of the radii of the Cu and the O atoms, indicating that the Cu atom might have formed a chemical bond with the surface O1 atom. The distance between Cu and Fe1 atoms increased to 2.675 Å, which was significantly larger than the bond length of Cu–O, indicating that the oxygen atoms on the specularite surface (0 0 1) had a stronger adsorption effect on Cu atoms of $\text{Cu}(\text{OH})^+$. At the same time, the distance between O1 atoms of $\text{Cu}(\text{OH})^+$ and Fe1 atoms on the specularite surface changed from 1.538 Å to 1.876 Å after optimization, which was smaller than the sum of the radii of Fe and O atoms. It shows that the adsorption of $\text{Cu}(\text{OH})^+$ on the surface was achieved not only by the bonding of Cu atoms in the $\text{Cu}(\text{OH})^+$ component with the surface O1 atoms but also by the bonding of O1 atoms with the surface Fe atoms. The adsorption energy of $\text{Cu}(\text{OH})^+$ on the specularite surface was calculated to be -0.85 eV. A negative value indicates that the adsorption of $\text{Cu}(\text{OH})^+$ on the (0 0 1) surface of specularite was spontaneous.

When $\text{Cu}(\text{OH})_2$ was placed on the specularite (0 0 1) surface (as shown in Figure 2d), the distances between Cu atoms of $\text{Cu}(\text{OH})_2$ and Fe1 and O1 atoms on the surface of specularite were 1.708 Å and 1.713 Å, respectively. In addition, the distance between O1 atoms of $\text{Cu}(\text{OH})_2$ and Fe1 atoms on the surface of specularite was 1.712 Å, and the distance between OII atoms and Fe5 atoms on the surface of specularite was 2.296 Å. After geometric optimization, the distances between the Cu atom of $\text{Cu}(\text{OH})_2$ and the surface O1 and Fe1 atoms increased to 2.146 Å and 2.750 Å, respectively. The distance between the Cu atom and the O1 atom was greater than the sum of its atomic radii, indicating that the Cu atom of $\text{Cu}(\text{OH})_2$ did not form a chemical bond with the surface O1 atom. While the distance between the O1 atom of $\text{Cu}(\text{OH})_2$ and the Fe1 atom on the specularite surface changed from 1.721 Å to 1.887 Å, and the distance between the OII atom and the Fe5 on the specularite surface had been reduced from 2.296 Å to 1.909 Å, both of which were smaller than the sum of the radii of Fe and O atoms, indicating that the adsorption of $\text{Cu}(\text{OH})_2$ on the specularite surface was mainly achieved by the bonding of OI and OII atoms of the $\text{Cu}(\text{OH})_2$ component with Fe1 and Fe5 on the specularite surface, respectively. The adsorption energy of $\text{Cu}(\text{OH})_2$ on the surface of specularite was calculated to be -1.78 eV. A negative value indicates that the adsorption of $\text{Cu}(\text{OH})_2$ on the specularite (0 0 1) surface was spontaneous.

The more negative the adsorption energy is, the stronger the adsorption capacity of the adsorbate on the mineral surface is [35–37]. Comparing the adsorption energy of Cu components on the surface of specularite, the results show that the adsorption energy of $\text{Cu}(\text{OH})_2$ component on the specularite (0 0 1) surface was the largest, followed by CuOH^+ and Cu^{2+} . Therefore, the adsorption stability of Cu species on the surface of specularite increased in the order of $\text{Cu}^{2+} < \text{Cu}(\text{OH})^+ < \text{Cu}(\text{OH})_2$.

3.3.2. Density of States Analysis of Interaction between Cu Species and Specularite (0 0 1) Surface

In order to further verify the interaction of Cu^{2+} , CuOH^+ , and $\text{Cu}(\text{OH})_2$ on the surface of specularite, the partial density of states (PDOS) of atoms of Cu components are shown in Figure 5. As shown in Figure 5, the PDOS of Cu atoms after adsorption on the specularite surface was composed of Cu 4s, Cu 2p, and Cu 3d orbitals. When Cu^{2+} adsorbed on the

specularite (0 0 1) surface (Figure 5a), the PDOS of the Cu atom near the Fermi level was contributed by the 4s, 2p, and 3d orbitals, in which the contributions of Cu 3d and 4s orbitals were strong, and that played an important role in the reactivity of Cu^{2+} adsorbed on the surface of specularite. Combined with the PDOS of Fe1 and O1 atoms on the surface of specularite (Figures 3b and 5a), it can be observed that the PDOS of the Cu 3d orbital peak at -1.3 eV and the Cu 2p orbital at 5 eV overlapped with the 2p orbital of the O1 atom on the specularite surface, indicating that Cu^{2+} mainly interacted with the O atoms on the surface of the specularite.

Figure 5. Partial density of states (PDOS) of different atoms of adsorbates: (a) Cu^{2+} , (b) Cu(OH)^+ , (c) Cu(OH)_2 .

When Cu(OH)^+ adsorbed on the specularite (0 0 1) surface (Figure 5b), the PDOS of the Cu 4s orbital peak near the Fermi level became weaker and shifted to the right, and the PDOS of Cu 4s orbital at 1.96 eV overlapped with that of the OI atom of Cu(OH)^+ . Combined with the PDOS of O1 atom on the specularite surface (Figure 4c), it was found that the 4s orbital of the Cu atom overlapped with the 2s orbital of O atom on the specularite surface, indicating that the Cu atom of Cu(OH)^+ may have interacted with the O atoms on the specularite surface. At the same time, by comparing the PDOS of OI atoms of Cu(OH)^+ with that of Fe1 atoms on the surface of specularite (Figures 3c and 5b), it can be seen that the new peaks appeared at -20 eV, which attributed to the Fe 4s and 3d orbital and overlapped with the OI 2p orbital, indicating that the OI atoms of Cu(OH)^+ interacted with the Fe atoms on the surface of the specularite, which further confirmed that the appearance

of new 4s orbital peaks of Fe atoms on the surface of specularite at -20 eV was caused by the adsorption of $\text{Cu}(\text{OH})^+$.

Similarly, when $\text{Cu}(\text{OH})_2$ adsorbed on the specularite (0 0 1) surface (Figure 5c), the PDOS of the Cu 4s orbital near the Fermi level disappeared, indicating that the contribution of the Cu 4s orbital to the activity of the Cu atom of $\text{Cu}(\text{OH})_2$ was reduced, and the activity of Cu atom was mainly contributed by the Cu 3d orbital. The PDOS of Cu atoms overlapped with two O atoms (OI and OII) of $\text{Cu}(\text{OH})_2$, and there was no obvious overlap compared with the PDOS of O atoms on the surface of specularite, indicating that Cu atoms did not interact with the O atoms on the surface of specularite. By comparing the PDOS of the OI atom with that of the Fe1 atom on the surface (Figures 3d and 5c), it is obvious that the two new Fe 4s orbital peaks and a new Fe 3d orbital peak of the Fe1 atom at -20 eV overlapped with the O 2s orbital of the OI atom, indicating that $\text{Cu}(\text{OH})_2$ was mainly absorbed on the specularite surface through the OI atom of $-\text{OH}$ interacting with the surface Fe atoms. This further confirmed that the appearance of two new 4s orbital peaks and a new 3d orbital peak of Fe atom on the specularite surface at -20 eV was caused by the adsorption of $\text{Cu}(\text{OH})_2$.

In summary, the adsorption of Cu species on the surface of specularite was different. Cu^{2+} may be adsorbed on the surface of specularite through the Cu atom directly interacting with O atoms to form Cu–O complexes, while $\text{Cu}(\text{OH})^+$ and $\text{Cu}(\text{OH})_2$ may be adsorbed on the surface of specularite through the interaction between OI (OII) atoms in $-\text{OH}$ and Fe atoms on the surface of specularite to form Cu–O–Fe complexes.

3.3.3. Interatomic Charge Transfer Analysis of Interaction between Cu Species and Specularite (0 0 1) Surface

Mulliken charge populations of bonding atoms before and after Cu species adsorption are shown in Table 4. The results show that the adsorption of adsorbates on the surface of specularite (0 0 1) led to a change in the charge of the bonding atoms and that the variation of them was in regard to Cu species. In the absence of an adsorbate on the surface, the charge of the Fe1 atom exhibited 0.86 e, in which Fe atoms lost electrons in the 4s and 2p orbitals and gained electrons in the 3d orbital; the charge of the O1 atom was -0.59 e, in which the O lost electrons in the 2s orbital and gained electrons in the 2p orbital, indicating that electrons were transferred from Fe atoms to O atoms to form Fe–O bonds. When Cu^{2+} adsorbed on the surface of specularite, the charge of Fe1 atom decreased from 0.86 to 0.68 e, with a decrease of 0.18 e; the charge of O1 atoms decreased from -0.59 to -0.62 e, with a decrease of 0.03 e. The electrons were obtained mainly in the O 2p orbitals, while the charge of the Cu atom was 0.50 e; the electrons were mainly lost in the Cu 4s orbitals compared with the charge before adsorption. Combining the above charge analysis between atoms, it is clear that the charges in the Cu–O1 bond formed by the adsorption of Cu^{2+} on the surface of specularite were mainly transferred from the 4s orbital of the Cu atom to the 2p orbital of the O1 atom.

When CuOH^+ adsorbed on the surface of specularite, the charge of surface Fe1 atom increased by 0.09 e from 0.86 to 0.95 e, where the main contributions of lost electrons were Fe 4s and Fe 2p orbitals. The charge of O1 atoms decreased by 0.05 e from -0.59 to -0.64 e, with the gained electrons mainly in the O 2p orbitals, while the charge of the Cu atom increased from 0.48 to 0.50 e, with the loss of electrons mainly in the Cu 4s orbital. In addition, the charge of the OI atom of $\text{Cu}(\text{OH})^+$ increased from -0.93 to -0.83 e, with the gain of electrons mainly in the OI 2p orbital. Combined with the above charge analysis between atoms, it is observed that the charges in the Cu–O1 bond formed after the adsorption of $\text{Cu}(\text{OH})^+$ were mainly transferred from the Cu 4s orbital to the O1 2p orbital and that the charges in the Fe1–OI bond formed were mainly transferred from the 4s and 2p orbitals of the Fe1 atom to the 2p orbital of the OI atom.

Table 4. Mulliken charge populations of bonding atoms before and after different Cu species adsorption.

Adsorbates	Atom		s	p	d	f	Total	Charge/e
Cu ²⁺	Cu	Before	1.00	0.00	10.00	0.00	11.00	0.00
		After	0.78	0.12	9.81	0.00	10.71	0.29
	Fe1	Before	0.40	0.24	6.49	0.00	7.14	0.86
		After	0.41	0.38	6.54	0.00	7.32	0.68
	O1	Before	1.88	4.71	0.00	0.00	6.59	−0.59
		After	1.86	4.76	0.00	0.00	6.62	−0.62
CuOH ⁺	Cu	Before	0.65	0.11	9.76	0.00	10.52	0.48
		After	0.53	0.17	9.79	0.00	10.50	0.50
	OI	Before	1.90	5.03	0.00	0.00	6.93	−0.93
		After	1.87	4.96	0.00	0.00	6.83	−0.83
	Fe1	Before	0.40	0.24	6.49	0.00	7.14	0.86
		After	0.27	0.32	6.45	0.00	7.05	0.95
	O1	Before	1.88	4.71	0.00	0.00	6.59	−0.59
		After	1.86	4.78	0.00	0.00	6.64	−0.64
Cu(OH) ₂	Cu	Before	0.62	0.09	9.44	0.00	10.16	0.84
		After	0.58	0.08	9.67	0.00	10.33	0.67
	OI	Before	1.90	4.98	0.00	0.00	6.87	−0.87
		After	1.87	4.94	0.00	0.00	6.81	−0.81
	OII	Before	1.90	4.99	0.00	0.00	6.88	−0.88
		After	1.86	4.96	0.00	0.00	6.83	−0.83
	Fe1	Before	0.40	0.24	6.49	0.00	7.14	0.86
		After	0.27	0.35	6.43	0.00	7.05	0.95
	O1	Before	1.88	4.71	0.00	0.00	6.59	−0.59
		After	1.87	4.76	0.00	0.00	6.62	−0.62

When Cu(OH)₂ adsorbed on the surface of specularite, the charge of surface Fe1 atoms increased from 0.86 to 0.95 e, with an increase of 0.09 e, in which the main contributions of lost electrons were Fe 4s and Fe 2p orbitals. The charge of O1 atoms remained essentially unchanged, indicating that the adsorption of Cu(OH)₂ had no significant effect on the charge of O1 atoms on the surface, which further confirms that the surface O1 atoms were not participating in the adsorption of Cu(OH)₂ on the specularite. The charge of the Cu atom decreased from 0.84 to 0.67 e, and the orbital lost electrons were mainly in Cu 4s, while the charges of OI and OII atoms increased from −0.87 and −0.88 to −0.81 and −0.83 e, with an increase of 0.06 e and 0.05 e, respectively, and the orbital gained electrons mainly in OI(OII) 2p. Combining the above charges between the atoms, it is clear that the charges in the Fe1–OI(OII) bond formed after the adsorption of Cu(OH)₂ were mainly transferred from the 4s and 2p orbitals of the Fe1 atom to the 2p orbitals of the OI(OII) atom. To further investigate the interaction between Cu components and the specularite surface, an electron density of different adsorbents adsorbed on the surface of specularite is shown in Figure 6, where different charge density is represented by different colors. Where the color goes from red to blue represents a gradual decrease in the ability of the atoms to gain electrons. The results in Figure 6 are consistent with the charge transfer results described above.

3.3.4. Analysis of Bond Properties of Cu Species Adsorbed on the Specularite Surface

The Mulliken bond population can reflect the strength of ionicity and covalency. The larger the bond population, the stronger the covalency, and the smaller the bond population, the stronger the ionicity [33,38,39]. In order to further understand the bonding properties between atoms in the specularite surface and Cu components, we compared the Mulliken bond populations of different Cu components adsorbed on the surface of specularite (0 0 1), as shown in Table 5.

Figure 6. Electron density of different adsorbents adsorbed on the surface of specularite: (a) Original, (b) Cu^{2+} , (c) $\text{Cu}(\text{OH})^+$, (d) $\text{Cu}(\text{OH})_2$.

Table 5. Mulliken bond populations of different Cu components adsorbed on the specularite (0 0 1) surface.

Adsorbates	Bond	Population
Cu^{2+}	O1–Cu	0.14
$\text{Cu}(\text{OH})^+$	O1–Cu	0.17
	OI–Fe1	0.33
$\text{Cu}(\text{OH})_2$	OI–Fe1	0.30
	OII–Fe5	0.30

When Cu^{2+} adsorbed on the specularite surface, the bond population of Cu–O1 was 0.14, which indicates that Cu–O had stronger ionicity and weaker covalency. When $\text{Cu}(\text{OH})^+$ adsorbed on the specularite surface, the bond populations of Cu–O1 and Fe1–OI were 0.17 and 0.33, respectively, indicating that Cu–O had stronger ionicity, while Fe–O had stronger covalency. When $\text{Cu}(\text{OH})_2$ adsorbed on the surface of specularite, the bond population of Fe1–OI(OII) was 0.30. It shows that Fe–O had stronger ionicity and weaker covalency. By comparing the Cu–O and Fe–O of the three Cu components on the surface of specularite (0 0 1), it can be seen that the bond population of Cu–O was smaller than that of Fe–O, indicating that the Cu–O was more ionic and Fe–O was more covalent.

4. Conclusions

In this work, the effect of Cu species adsorption on the crystalline structure and properties of specularite (0 0 1) was investigated by DFT calculations. Additionally, the activation mechanism of Cu^{2+} on the flotation of specularite was discussed based on

analyses of the adsorption model, adsorption energy, partial density of states (PDOS), charge transfer, and bond properties. Based on the defined methods of analysis and the obtained results, it can be concluded:

- (1) The results of crystalline structure and electronic properties of a specularite (0 0 1) surface show that the geometric structure and electronic properties of the surface of specularite (0 0 1) are significantly changed after absorbing the Cu species, and the structure of O3–Fe1–O1 near the absorbate is more easily affected.
- (2) The results of adsorption energy analysis show that Cu^{2+} , $\text{Cu}(\text{OH})^+$, and $\text{Cu}(\text{OH})_2$ can be spontaneously adsorbed on the surface of specularite (0 0 1), and the adsorption stability of Cu components that are on the surface of specularite increase in the order of $\text{Cu}^{2+} < \text{Cu}(\text{OH})^+ < \text{Cu}(\text{OH})_2$.
- (3) The results of the adsorption module and PDOS analysis show that the adsorptions of Cu species on the surface of specularite are different. Cu^{2+} may be adsorbed on the surface of specularite through a Cu atom directly interacting with O atoms to form Cu–O complexes, while $\text{Cu}(\text{OH})^+$ and $\text{Cu}(\text{OH})_2$ may be adsorbed on the surface of specularite through the interaction between OI (OII) atoms in –OH and Fe atoms on the surface of specularite to form Cu–O–Fe complexes.
- (4) The results of charge transfer analysis show that the charges in the Cu–O bond formed after the adsorption of absorbates were mainly transferred from the Cu 4s orbital to the O 2p orbital and that the charges in the Fe–O bond formed were mainly transferred from the 4s and 2p orbitals of the Fe atom to the 2p orbital of the O atom.
- (5) By comparing Cu–O and Fe–O of the three Cu components on the surface of specularite (0 0 1), it can be seen that the bond populations of Cu–O are smaller than those of Fe–O, indicating that Cu–O is more ionic and Fe–O is more covalent.

Simply, the adsorption effects of various Cu species on a specularite (0 0 1) surface are obviously different. At pH = 7, the formation of Cu–O and Cu–O–Fe complexes increase the adsorption sites for sodium oleate on a specularite surface of Cu^{2+} -modified specularite. More hydrophobic substances were formed on the surface, which improves the floatability of specularite.

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