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Density functional theory study of H₂O adsorption on different sphalerite surfaces

Zheng-bin Deng ^{1,2,3,4}, Xiong Tong ^{4,5}, Ling-yun Huang ^{4,5}, Xian Xie ^{4,5}

¹ Mining College, Guizhou University, Guiyang 550025, Guizhou, China

² National & Local Joint Laboratory of Engineering for Effective Utilization of Regional Mineral Resources from Karst Areas, Guizhou University, Guiyang 550025, Guizhou, China

³ Guizhou Key Lab of Comprehensive Utilization of Non-metallic Mineral Resources, Guizhou University, Guiyang 550025, Guizhou, China

⁴ State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming 650093, China

⁵ Faculty of Land and Resource Engineering, Kunming University of Science and Technology, Kunming 650093, China

Corresponding author: 12607199@qq.com (Ling-yun Huang)

Abstract: Effects of In, Ge, Fe substitution in the lattice of sphalerite on wettability were usually ignored, therefore the optimal flotation condition could be difficult to find due to lacking of sufficient theoretical study on water adsorption, resulting lower recoveries of different sphalerites. Adsorption of H₂O on different sphalerite surfaces was studied using density functional theory (DFT) method. All computational models were built in a vacuum environment to eliminate the effects of oxygen and other factors. H₂O molecule prefers to stay with ideal sphalerite, indium-beard sphalerite, germanium-beard sphalerite and marmatite surfaces rather than water. Compared with ideal sphalerite surface, Fe atom improves the hydrophilicity of surface, while In and Ge atoms reduce the hydrophilicity.

Keywords: density functional theory, sphalerite, water adsorption, hydrophobicity

1. Introduction

Deposit of rare metals resources in the earth's crust is very scarce, where indium and germanium are usually limited. The two elements are of non-renewable important strategic resources and widely used in high-tech fields like electronics, semiconductor, known as the "high-tech" elements (Alfantazi and Moskalyk, 2003). The main carrier minerals of indium and germanium in complex polymetallic sulfide ore are in the forms of different sphalerites, called as "indium-beard sphalerite and germanium-beard sphalerite" respectively, always coexists with other sulphide minerals, such as copper and lead sulfide minerals.

Froth flotation is an important mineral processing method of sphalerite, including indium-beard sphalerite and germanium-beard sphalerite, which takes advantage of the differences in wettability at mineral particle surface to concentrate the value minerals (Hu, 2014). Thus, water adsorption on sulfides surfaces determined by the hydrophobic or hydrophilic nature of the solids at the solid-liquid-gas interfacial region is very important in froth flotation.

In the last study, the fundamentals of water interaction with solid surfaces were studied, which define two principal mechanisms of water adsorption as involving either associative or dissociative surface interaction (Fuerstenau and Sabacky, 1981). However, the detailed analysis of water-sulphide interactions is rare. In recent years, density functional theory (DFT) has become a powerful tool for studying surface structures and surface interactions from a microscopic aspect. Chen et al. (2010) carried out DFT calculations to investigate the effect of lattice impurities on the electronic structures and flotability of sphalerite. Liu et al. (2010) study on surface atomic relaxation properties and dissolubility of natural sphalerite. Long et al. (2016) conducted a DFT study on the adsorption of ethyl xanthate on a ZnS (110) surface in the presence of water molecules. Zhao et al. (2014) conducted a DFT study on the

adsorption of water on pyrite, sphalerite, galena and molybdenite surfaces. However, these simulations just took ideal sphalerite as the study subject. Our research (Deng et al., 2015) found that the indium and germanium-beard sphalerites have different character and flotability from ideal sphalerite. Becker et al. (2001, 2003) also found that the chemical reaction of one surface site influences the electronic structure and reactivity of neighboring or nearby sites. Therefore, it is necessary to ascertain the interaction mechanisms of indium-beard sphalerite, germanium-beard sphalerite and marmatite surfaces with water molecules.

In this work, H₂O adsorption on sphalerite surfaces and the natural hydrophobicity of sulfide minerals were studied by density functional theory (DFT) method. The sulfide minerals studied included ideal sphalerite, indium-beard sphalerite, germanium-beard sphalerite and marmatite. All calculations were carried out in the vacuum environment to completely eliminate the effects of oxygen and other similar factors.

2. Computational and experimental methods and models

2.1. Computational method

Based on the DFT method, all calculations were performed by CASTEP (Cambridge serial total energy package) program module developed by Payne et al (1992), which is a first-principle pseudopotential method based on DFT. The DFT calculations have been performed using plane wave (PW) basis sets and ultrasoft pseudopotentials (Vanderbilt, 1990). The exchange correlation functional used was the generalized gradient approximation (GGA), developed by Perdew and Wang (1992) (PW91). The interactions between valence electrons and ionic core were represented with ultrasoft pseudopotentials. Valence electrons configuration considered in this study included Zn 3d 4s 3p, Ge 4s 4p, In 4d 5s 5p, and Fe 3d 4s 3p states. Based on the test results, K-point was 3×4×1, a plane-wave cutoff energy of 340 eV was used in all calculations. The thicknesses of vacuum layer are 12 Å, which is the most stable. The convergence tolerances for geometry optimization calculations were set to be the maximum displacement of 0.002 Å, the maximum force of 0.08 eV/Å, the maximum energy change of 2.0×10⁻⁵ eV/atom and the maximum stress of 0.1 GPa, and the self-consistent field (SCF) convergence tolerance was set to be 1.0×10⁻⁵ eV/atom.

2.2. Computational model

Ideal sphalerite has cubic crystal structure with space group of F-43m with surface (110). Each Zn atom of the surface coordinates with three S atoms, while each S atom coordinates with two Zn atoms and one S atom (Fig. 1). Zn atom of T site will be replaced by In, Ge or Fe atom to form indium-beard sphalerite, germanium-beard sphalerite and marmatite surfaces (CHen et al., 2010). One or two water molecules were put in a vacuum cell volume of 15×15×15 Å, BFGS algorithm was used to optimize its structure. All surfaces were obtained with the optimum unit cell volume and were modeled using a supercell approach (2×2×1), where the central cell, periodic in 3D, contains a slab with two surfaces and a vacuum gap above and below the surfaces separating adjacent mirror images of the slab. The surface energies of a range of surfaces with varying slab thicknesses were calculated to determine the slab size. Fig. 1 is the most stable slab models resulted from DFT calculations. During all geometry optimization calculations, the lower three atomic layers of the slab were kept fixed to prevent the slab from drifting vertically along the supercell.

2.3. Calculation of adsorption energy and heat

The adsorption energies of H₂O on sulfide surfaces are calculated as

$$E_{\text{ads}} = E_{\text{H}_2\text{O}/\text{surface}} - E_{\text{H}_2\text{O}} - E_{\text{surface}} \quad (1)$$

where E_{ads} is the adsorption energy; $E_{\text{H}_2\text{O}}$ is the energy of the H₂O molecules calculated in a cubic cell; E_{surface} is the energy of the sphalerite, indium-beard sphalerite, germanium-beard sphalerite and marmatite slab; $E_{\text{H}_2\text{O}/\text{surface}}$ is the energy of the of the four sphalerite slabs with adsorbed H₂O.

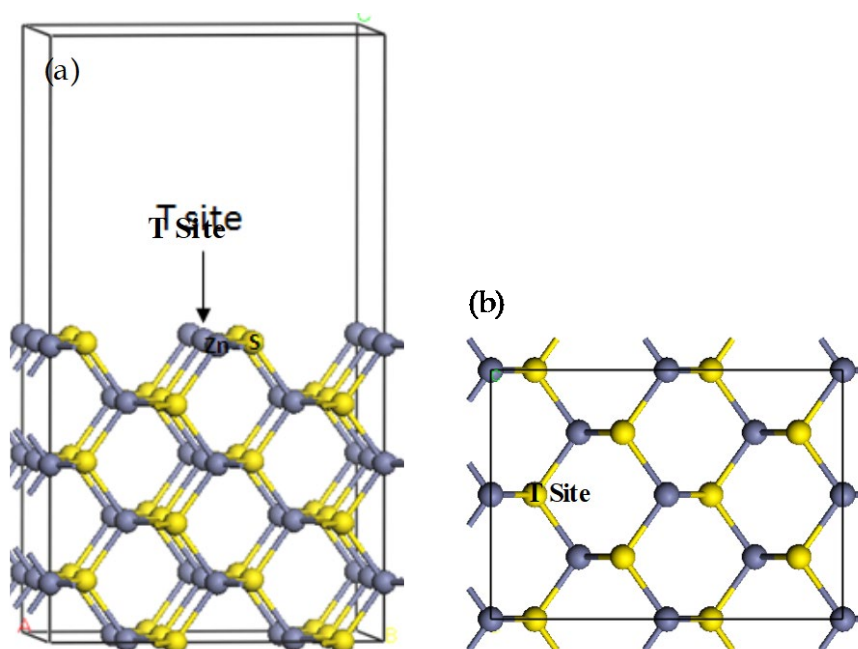


Fig. 1. Slab models of ideal sphalerite (110) surface, (a) - side view (b) - top view

3. Results and discussion

3.1. Interaction between water and sphalerite surfaces

There are many adsorption sites for H₂O interaction with sulfide surface. Each adsorption site would provide a lot of important information. To determine the optimal adsorption site of H₂O on sulfide surfaces which is the most stable structure, adsorption site and adsorption configuration were examined. The calculation results show that the interaction between oxygen of H₂O molecules and metal atom of mineral surfaces is the strongest. Fig. 2 shows the adsorption models of H₂O molecules on the surface of sphalerite, indium-bearing sphalerite, germanium-bearing sphalerite and marmatite, which are the most stable adsorption configuration through optimization test of various adsorption sites. It is obviously observed from the models in Fig. 2 that H₂O molecules show significantly different adsorption modes on various minerals surfaces.

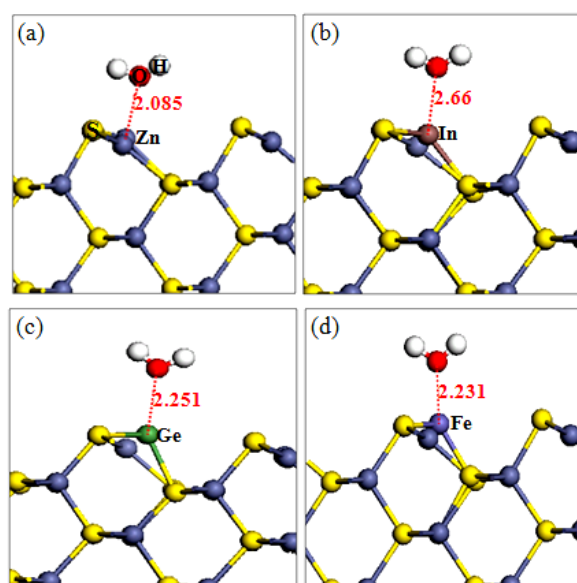


Fig. 2. The equilibrium adsorption of H₂O on different sphalerite (110) surfaces, (a) - ideal sphalerite, (b) -indium-bearing sphalerite, (c) - germanium-bearing sphalerite, (d) - marmatite

Table 1 presents the distance changes between O atoms of H₂O molecules and adsorption atom (metal) of minerals surfaces (d_{ads}) compared with the sum of the atomic radius of O atom and adsorption atom (d_0). After adsorption, the distance between O of H₂O molecules and adsorption atoms of marmatite and sphalerite surfaces obviously decreases (-0.139 Å and -0.095 Å), indicating that the strong interaction takes place between H₂O and marmatite and sphalerite surfaces. Whereas for the other two sphalerites (indium-beard sphalerite and germanium-beard sphalerite), the distances between O atoms of H₂O molecules and adsorption atoms of surfaces after adsorption increased slightly. Between them, the distance change between O atoms of H₂O molecules and adsorption atoms (Ge and In) of surfaces are 0.081 Å and 0.01 Å respectively, suggesting that interactions between H₂O molecules and the two sphalerite surfaces are weak.

To evaluate the strength of interactions between H₂O molecules and sulfide surfaces, the changes of H-O-H angle and H-O bond length of H₂O molecules on sulfide surfaces before and after adsorption were calculated and the data are presented in Table 2. The change of H-O-H angle of H₂O adsorbed on marmatite surface is the largest, and increases from 104.422° to 106.961°, then is sphalerite, while change of H-O bond length of H₂O adsorbed on marmatite surface is also the largest, from 0.977 Å to 0.989 Å. These results confirm the strong interaction between H₂O and the surface of marmatite and sphalerite. The changes of H-O-H angle and H-O bond length of H₂O adsorbed on indium-beard sphalerite and germanium-beard sphalerite surfaces are relatively small, indicating the weak interaction between H₂O and the surfaces.

Table 1. Variations of distance between O atoms of H₂O and metal atoms of sphalerite surfaces after adsorption

| Surfaces | $d_0(=r_0+r_{\text{metal}})/\text{Å}$ | $d_{\text{ads}}/\text{Å}$ | $\Delta d(=d_{\text{ads}}-d_0)/\text{Å}$ |
|----------------------------|---------------------------------------|---------------------------|--|
| Ideal sphalerite | 2.18 | 2.085 | -0.095 |
| Indium-beard sphalerite | 2.65 | 2.660 | 0.010 |
| Germanium-beard sphalerite | 2.17 | 2.251 | 0.081 |
| Marmatite | 2.37 | 2.231 | -0.139 |

r_0 is atomic radius of O for H₂O; r_{metal} is atomic radius of metal for surfaces; d_{ads} is the distance between O atom of H₂O and metal atom of mineral surfaces after adsorption.

Table 2. Variations of H-O-H angle and H-O bond length of H₂O molecule on different sphalerite surfaces before and after adsorption.

| Surfaces | Before adsorption | | After adsorption | |
|----------------------------|-------------------|-------------------|------------------|-------------------|
| | H-O-H angle /° | O-H bond length/Å | H-O-H angle /° | O-H bond length/Å |
| Ideal sphalerite | 104.422 | 0.977 | 105.359 | 0.981 |
| Indium-beard sphalerite | 104.422 | 0.977 | 105.180 | 0.978 |
| Germanium-beard sphalerite | 104.422 | 0.977 | 104.389 | 0.960 |
| Marmatite | 104.422 | 0.977 | 106.961 | 0.989 |

3.2. Adsorption energies of H₂O molecules on sphalerite surfaces

Table 3 shows the adsorption energies of H₂O molecules on the surfaces of various sulfide minerals (E_{ads}). The data reveal that the adsorption energy of H₂O on the marmatite surface is the lowest, -1.98 eV; then sphalerite, -1.94 eV; germanium-beard sphalerite -1.29 eV and indium-beard sphalerite -1.01 eV (negative sign represents exothermic reaction). The adsorption energy of H₂O on the sphalerite surface at low coverage by ZHAO et al (Zhao et al., 2014) is -0.251 eV, which is slightly lower than our result. The smaller adsorption energy may be due to different parameters used in the calculations by ZHAO et al, such as cut-off energy and vacuum layer. In fact, there also exist interactions between H₂O molecules that affect the adsorption of a H₂O molecule toward the mineral surfaces. The binding energy between H₂O molecules ($E_{\text{H}_2\text{O}-\text{H}_2\text{O}}$) was calculated to be -0.2 eV. The data show that the adsorption energies of H₂O molecules on the four mineral surfaces are lower than binding energy between H₂O molecules. The lower adsorption energy favors H₂O molecule to interact with the surface of four minerals. It is obvious that they are all hydrophilic, Fe atom improves the hydrophilicity, while In and Ge atoms reduce the hydrophilicity of sphalerite surface. According to the single minerals flotation results (Fig. 3), it shows that the natural flotation ability of four sphalerites was very poor without any reagents. The recovery of sphalerite is the highest, and follow by germanium-beard sphalerite, indium-

beard sphalerite and marmatite under the same condition. The flotation results are consistent with the conclusion of calculation results of that they are all hydrophilic, so they were very difficult to be floated out. But the different surfaces led to the different floatability.

Table 3. Adsorption energy of H₂O molecules at sphalerite surfaces (eV)

| Surfaces | Adsorption energy | | | E _{H₂O-H₂O} | E _{ads} |
|----------------------------|----------------------|-------------------------------------|-----------------------------|--|------------------|
| | E _{surface} | E _{H₂O/surface} | E _{H₂O} | | |
| Ideal sphalerite | -47738.43 | -47777.65 | -468.72 | -0.2 | -1.94 |
| Indium-beard sphalerite | -47588.60 | -47626.62 | -468.72 | -0.2 | -1.01 |
| Germanium-beard sphalerite | -46135.20 | -46135.20 | -468.72 | -0.2 | -1.29 |
| Marmatite | -46890.87 | -47361.57 | -468.72 | -0.2 | -1.98 |

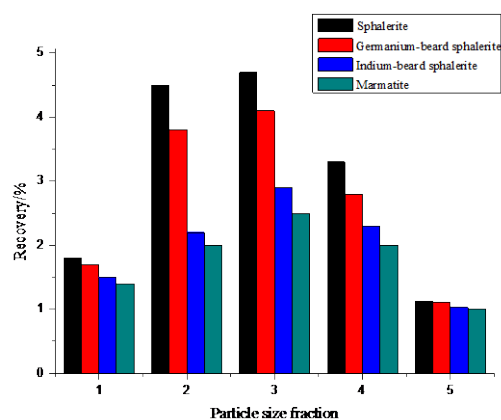


Fig. 3 The natural floatability results of different particle sphalerite

3.3. Electron density of H₂O molecules on sphalerite surfaces

Fig. 4 presents the electron density of sphalerite (110) surface after H₂O adsorption. Electron density maps can clearly analyze the interatomic bond characteristics among O, Zn, In, Ge and Fe atoms. As shown in Fig. 4, the white areas denote that the surface charge density is 0 eV, and the numbers in the diagram indicate the size of the bond populations. The stronger the bond population is, the greater the covalent bond is. If the bond population is larger than 0, the main interaction is covalent bond. Conversely, if the bond population is smaller than 0, the main interaction is ionic bond (SEGALL et al., 1996). After adsorption, Fig. 4d shows that an overlap of a small amount of electron cloud between O and Fe atom of marmatite surface obviously occurs at the edges, and the bond population is 0.22, indicating that the strong interaction takes place between H₂O and marmatite surface, and the absorption of H₂O on surface is covalent bond. Compare it, the electron cloud between O and Zn atoms overlap slightly, and the bond population is 0.08, suggesting weaker interactions between H₂O molecules and sphalerite surface. Whereas for the other two sulfides (indium-beard sphalerite and germanium-beard sphalerite), the bond populations between O atoms of H₂O molecules and adsorption atoms of all sulfide surfaces after adsorption approximate to 0. Between them, bond populations between O atoms of H₂O molecules and indium-beard sphalerite surface is the larger (-0.02) than germanium-beard sphalerite (-0.15), suggesting that they do not form a covalent bond, and the absorption of H₂O on the surfaces are ionic bond.

3.4. Density of states of surface atoms

Fig. 5 shows DOS results of metal atoms of sulfide surfaces. The position of Fermi level is 0. For metal and semiconductor, significantly physical processes occur in the vicinity of Fermi level. In other words, DOS at Fermi level represents atomic reaction activity. It is observed from Fig. 4 that near Fermi level, the electrons of H₂O are from O 2p orbital, while electrons of sphalerite, germanium-beard sphalerite,

indium-beard sphalerite and marmatite surfaces are mainly from the Zn 3d and 3p, Ge 4s and 4p, In 5s and 5p, and Fe 4s, 3p and 3d orbitals, besides, their DOS is large at Fermi level, which indicates that these sulfides surfaces are active. Hence, it is easy for them to react with H₂O or absorb H₂O on the surfaces. After H₂O adsorb on the surfaces, the DOS curve of O shifts to a lower energy level and the electrons at Fermi level is close to zero, suggesting that O atom electronic nonlocality is enhanced and H₂O molecules become very stable. However, the shape of DOS curve of Zn, Ge, In and Fe changes slightly after H₂O adsorption, a new density peak of Zn, In and Ge appears at -5 eV, -6.3 eV and -4.9 eV respectively, indicating that the hybridization turn away from Fermi level and there are weak hybridization. Compared with other three atoms, a new density peak of Fe appears at Fermi energy level, As a result, the interaction between H₂O and marmatite surfaces are stronger than that between H₂O and sphalerite, germanium-beard sphalerite and indium-beard sphalerite, which is in good agreement with its hydrophilicity.

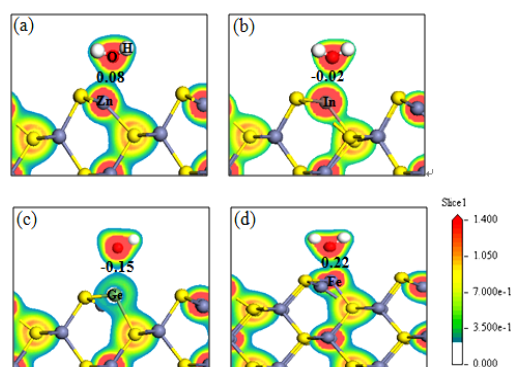


Fig. 4. Electron density of different sphalerite (110) surfaces after H₂O adsorption, (a) - ideal sphalerite, (b) - indium-beard sphalerite, (c) - germanium-beard sphalerite, (d) - marmatite

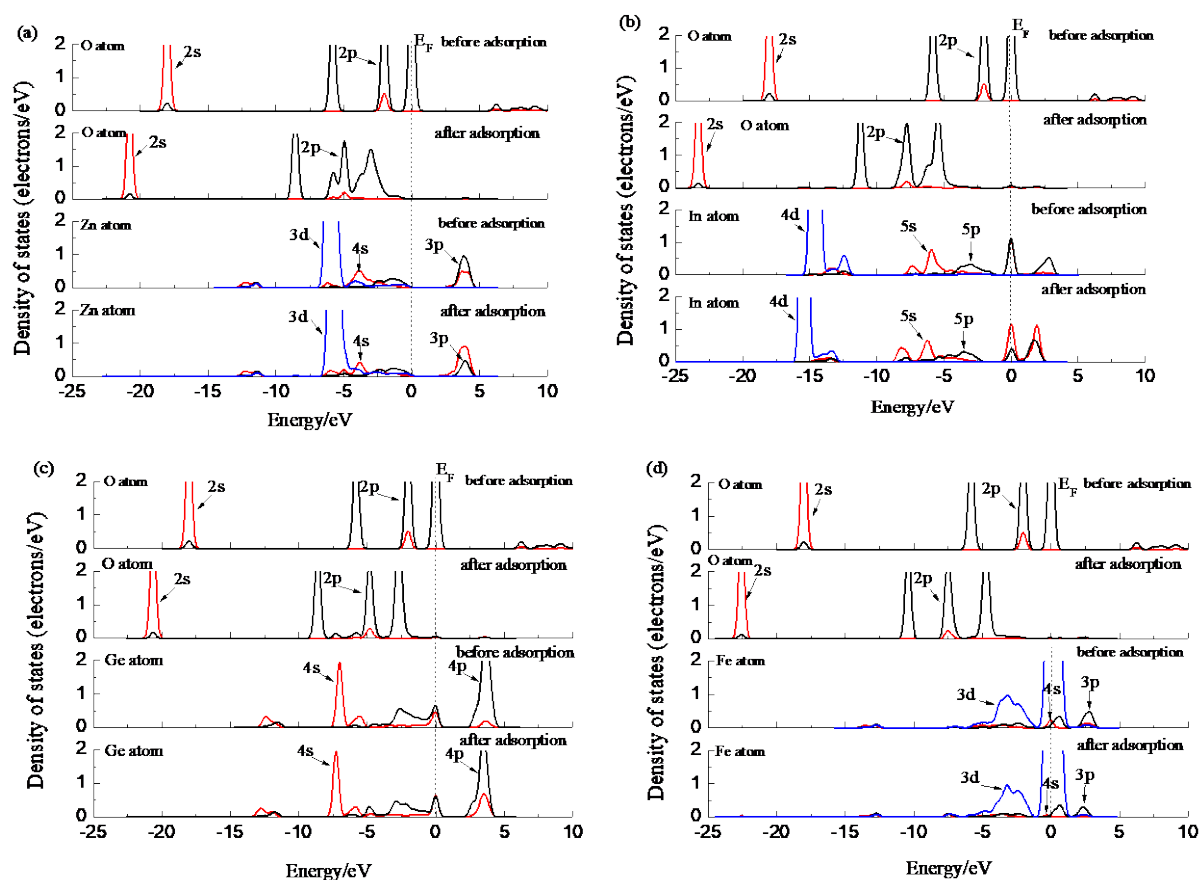


Fig. 5. Density of states of O, Zn, In, Ge and Fe tom before and after H₂O adsorption on different sphalerite (110) surfaces, (a) - ideal sphalerite, (b) - indium-beard sphalerite, (c) - germanium-beard sphalerite, (d) - marmatite

4. Conclusions

1) After adsorption, the distance between O of H₂O molecules and adsorption atoms of marmatite and sphalerite surfaces obviously decreases, whereas for the indium-beard sphalerite and germanium-beard sphalerite, the distances between O atoms of H₂O molecules and adsorption atoms of surfaces increase slightly.

2). Four sphalerites are all hydrophilic, H₂O molecule prefers to stay with the four sphalerite surfaces rather than water. Fe atom improves the hydrophilicity, while the In and the Ge atoms reduce the hydrophilicity of sphalerite surface.

3). H₂O molecule adsorbs on Zn and Fe atoms of sphalerite surfaces by covalent bond, while on In and Ge atoms of indium-beard sphalerite and germanium-beard sphalerite by ionic bond.

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