DFT research on activation of sphalerite[①]

SUN Wei(   ), HU Yue-hua(   ), QIN Wen-qing(   )

(School of Mineral Processing and Bio-engineering, Central South University,
Changsha 410083, China)

Abstract: Activation of sphalerite ZnS, (Zn, Fe)S, (Zn, Cu)S were carried out using the density functional theory (DFT) method. The electronic structures and related properties of three kind of zinc sulfide compounds were investigated. In addition, the relation between electronic structure and flotation behavior was discussed. The results show that, ZnS has a broader band gap than (Zn, Cu)S and (Zn, Fe)S do, and it has low electrochemistry activity to react with flotation collectors to render the surface hydrophobic. When the Zn atom in ZnS is replaced by Cu atom, the band gap will be reduced, and the top valence band will be occupied by Cu 3d orbit, thus it is beneficial to the interaction between mineral surface and collector.

Key words: density functional theory(DFT); sphalerite; marmatite; activation; flotation

CLC number: TD 925.5   **Document code:** A

1 INTRODUCTION

Sphalerite, which is also known as blende, is an important mineral of zinc. Most natural sphalerites contain iron more or less in lattice depended on chemistry environment and temperature[1]. High-iron-content sphalerite is called marmatite. Some works show that the presence of Fe in the sphalerite lattice is thought to have a significant effect on the surface properties of ZnS minerals[2–4].

In general, sphalerite has a poor flotation response to xanthate collectors due to the solubility of Zn-xanthate species, but it can be activated by other transition metal ions such as Cu(II), Pb(II), Ag(I), Au(I), Cd(II) and Fe(II)[5,6]. Activating behavior of Cu^{2+} on ZnS has been investigated extensively[7–9]. During activation, it is generally accepted that Cu^{2+} ion[10,11] can replace Zn^{2+} ion at the mineral surface and the xanthate collector will react with the Cu ions, but we are not sure why (Zn, Cu)S is easier to be floated than ZnS.

Although sulfide flotation process has been studied extensively, it is still not clear. It is complicated and involves a lot of affecting factors including surface property and reaction at mineral surface. Salamy and Nixon[12] proposed a model based on mixed-potential theory. In this model, the oxidation of mineral surface or xanthate was accompanied by the reduction of dissolved oxygen. This kind of electrochemistry reaction made sulfide floatable. The model does not take the semiconductor property of sulfide into account. Plaskin proposed that the adsorption of O_2 on sulfide surface would convert the surface from N-type to P-type by electron trapping. The P-type surface is apt to adsorb flotation reagent.

The semiconductor properties of ZnS and transition metal doped ZnS has been extensively studied because these materials are commercially used in phosphor and also in thin-film electroluminescence devices[13–19]. Recently, iron or zinc sulfides have attracted particular interest in the field of solar energy conversion owing to their favorable absorption coefficients and energy gap characteristics. Their works show that doped ions can dramatically change the surface properties of ZnS and form a new class of luminescent.

One approach of better understanding of the properties of solid is to model the electron structure with quantum mechanical methods. In order to gain an insight into the physical and chemical properties of the surface, it is necessary to know the bulk and surface material properties.

In this study, the authors employ density functional theory (DFT) to calculate the electron structures of sphalerite, marmatite and (Zn, Cu)S in order to investigate the effect of Cu and Fe ions on the semiconductor properties of ZnS, and then to discuss the mechanism of activation flotation of sphalerite.

2 MODEL OF CALCULATION

The electric-structure calculation presented here was performed using CASTEP computer code, which is based on density functional theory, aided by the CERIUS2 graphical front-end. The wave functions

were expended in a plane wave basis set, and the effective potential of ions was described by ultrasoft pseudopotentials.

Structure of sphalerite and marmatite is analogous to the diamond structure, as shown in Fig. 1. The structure is a unit cube with zinc atoms at the corners and face centers. The space group of sphalerite and marmatite is F-43m. The initial ZnS lattice parameter used in calculation is $a = 0.543$ nm. The distance between sulfur and neighbor zinc is 0.234 nm and the distance between two neighbor S or Zn atom is 0.383 nm. The pseudopotentials were tested by optimizing the structure of bulk ZnS and comparing with the experimental data. In the structure optimization, the generalized gradient approximation (GGA)-PW91 is used for exchange-correlation function.

In optimization of the bulk structure, the cell parameters for DFT calculations were in good agreement with those found experimentally. For ZnS and marmatite, a is 0.541 nm and 0.542 nm, respectively, while the experimental values are 0.540 6 nm and 0.542 5 nm (H. M. Steele2003). Optimized cell parameters of ZnCuS is 0.543 nm. The data for ZnS and ZnFeS have proved that the DFT methods is accurate enough. In marmatite or ZnCuS, one Zn atom displaced by Fe or Cu atom, and the substituting percentage is 25%.

3   CALCULATION RESULTS

The energy bands of frontier electrons in semiconductors consist of a valence band fully occupied by electrons at low levels, a vacant conduction band at high energy levels; and a forbidden band called the band gap which separates the former two bands. Fig.

2 shows the calculated band structure of sphalerite along selected high-symmetry lines within the first Brillouin zone of FCC lattice. The corresponding total density of state(DOS) is also shown in Fig. 2 and partial DOS of every element is shown in Fig. 3. The results are in good agreement with other DFT works[20, 21]. In Fig. 2, the band gap is calculated to be 2.4 eV. It is smaller than the experimental band gap, which is measured to be 3.6 eV[22]. The valance band of sphalerite has been studied by using X-ray photoemission spectra (XPS)[23, 24]. Their spectra show the features that can be recognized in the calculated DOS in Fig. 3. The S 3s orbit is located in the interval from −14.5 eV to −12.5 eV. This is in agreement with the works reported by Santoni et al[25]. Fig. 3 shows some hybridization of Zn 3s, 3p and S 3p orbits in the interval from 0 to −5 eV, which is the area of Zn—S bond. The bottom of the conduction band is a mixture of Zn 4s and S 3p orbits, because it derived from Zn—S antibond.

The calculated band structure of marmatite is shown in Fig. 4. The corresponding total density of state(DOS) is also shown in Fig. 4 and partial DOS of every element is shown in Fig. 5. It can be seen that when the Zn atom is replaced by Fe atom, the band gap reduces (0.5 eV), and this phenomenon is in good correspondences with researches of Kashyout et al[26, 27] (< 0.6 eV). Fe 3d and S 3p occupy the top of the valence band implying that there is bonding between Fe and S atom. The bottom of the conduction band is composed of S 3s and S 3p. The peaks in the interval from −2 eV to −8 eV come from S 3p orbit. The Zn 3d orbit in marmatite is located at the interval around −7.5 eV. The S s orbit below the valence band is divided into two energy intervals from −13 eV to −15 eV and from 0 eV to −5 eV.
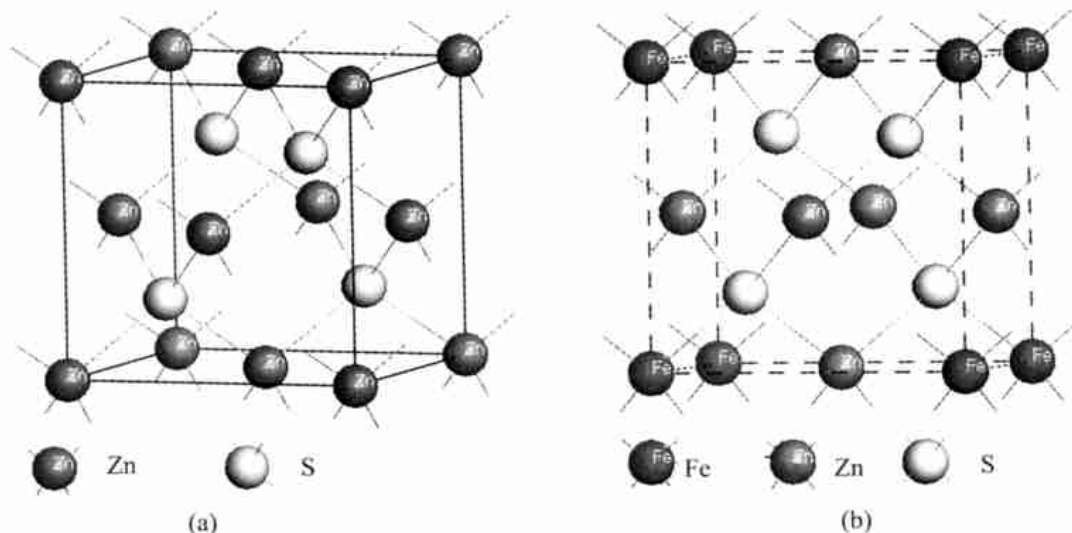

Fig. 1   Crystal structure of sphalerite and marmatite
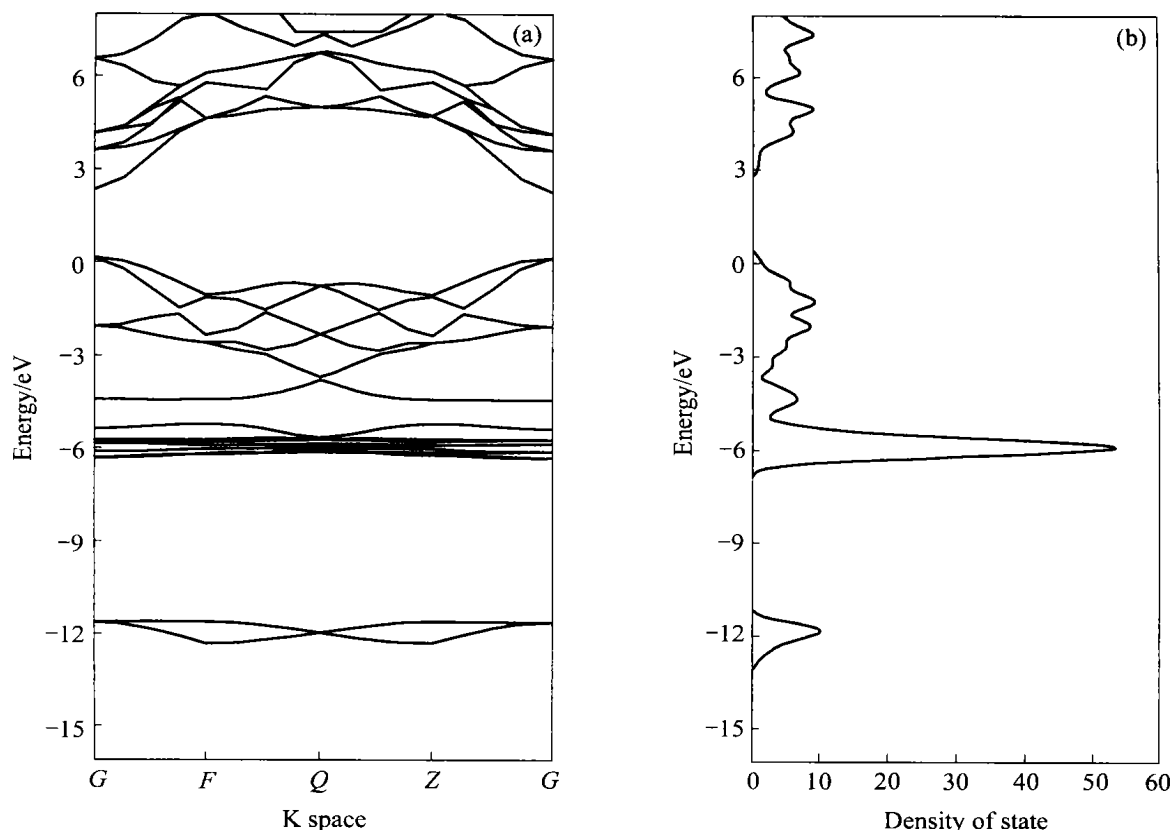(a)−Sphalerite; (b)−Marmatite

Fig. 2 Calculated band structure(a) and corresponding total density of state(b) of sphalerite
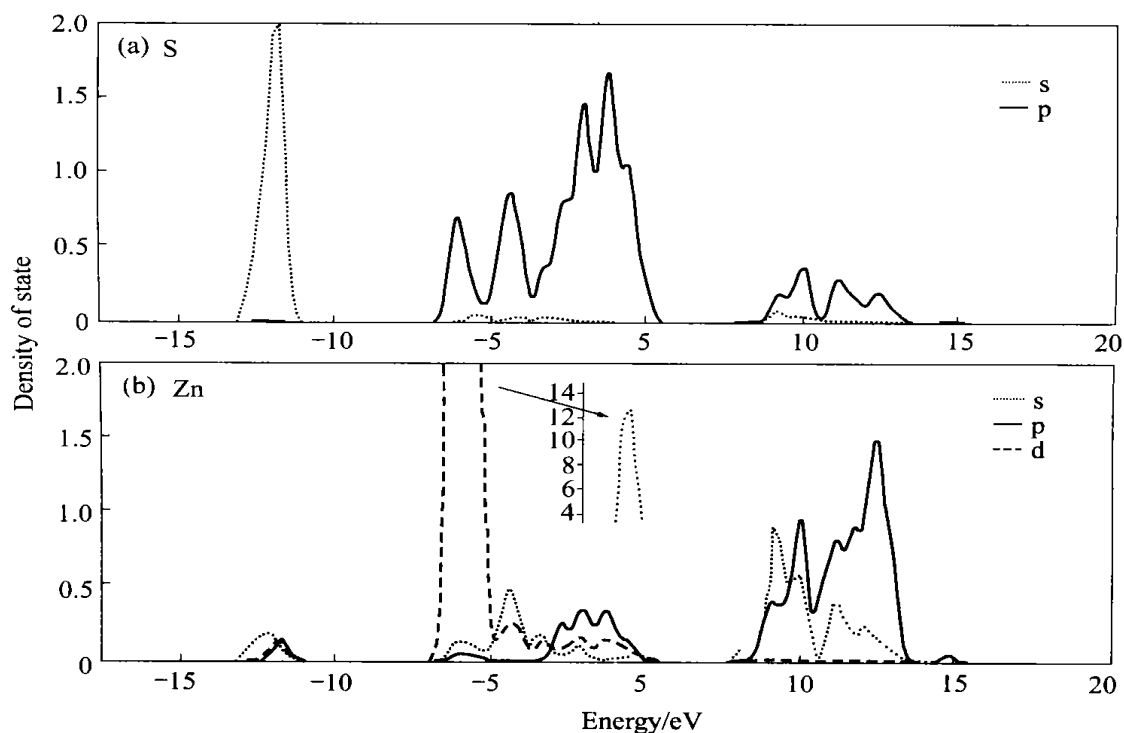

Fig. 3 Calculated partial density of state of elements in ZnS

The main features of (Zn, Cu)S band structure are given in Fig. 6. The corresponding total density of state (DOS) is also shown in Fig. 6 and partial DOS of every element is given in Fig. 7. Compared with Fig. 2 and Fig. 4, ZnCuS has a band gap(1.6 eV)

larger than marmatite does and less than sphalerite does. Most of states in valence band which is located from −5 eV to 0 eV are occupied by Cu 3d orbit, and only a handful of them are occupied by Zn 4p and S 3p orbits. Other peaks in Fig. 7 can also be seen in
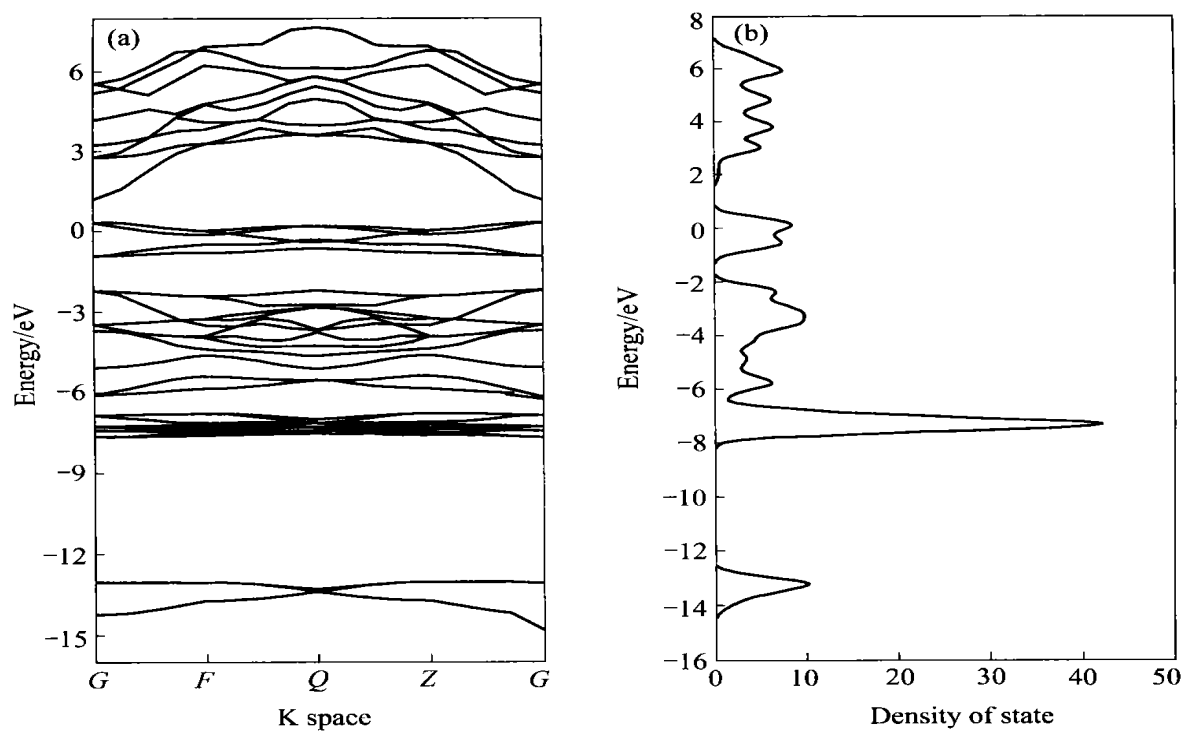
Fig. 4 Calculated band structure(a) and corresponding total density of state(b) of marmatite
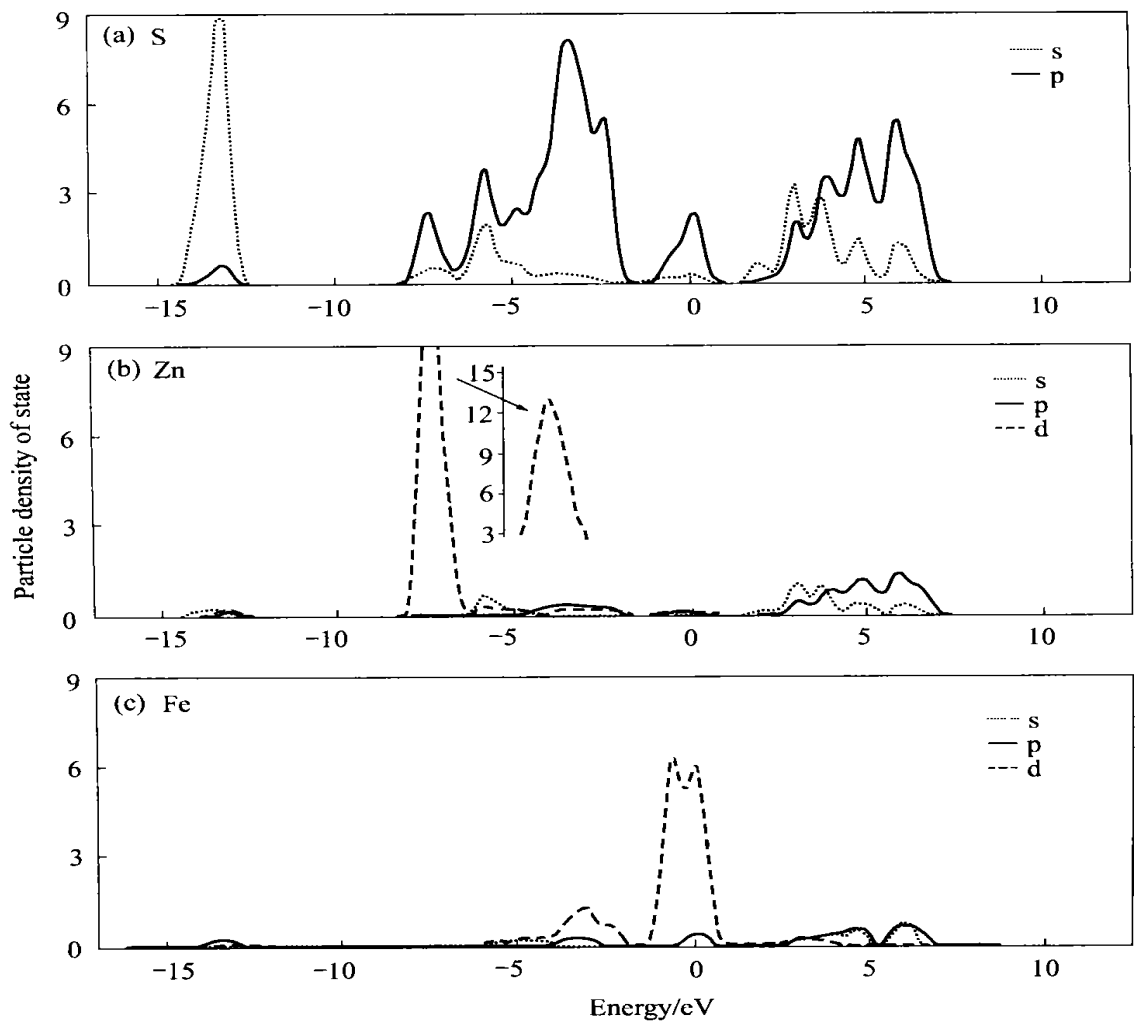

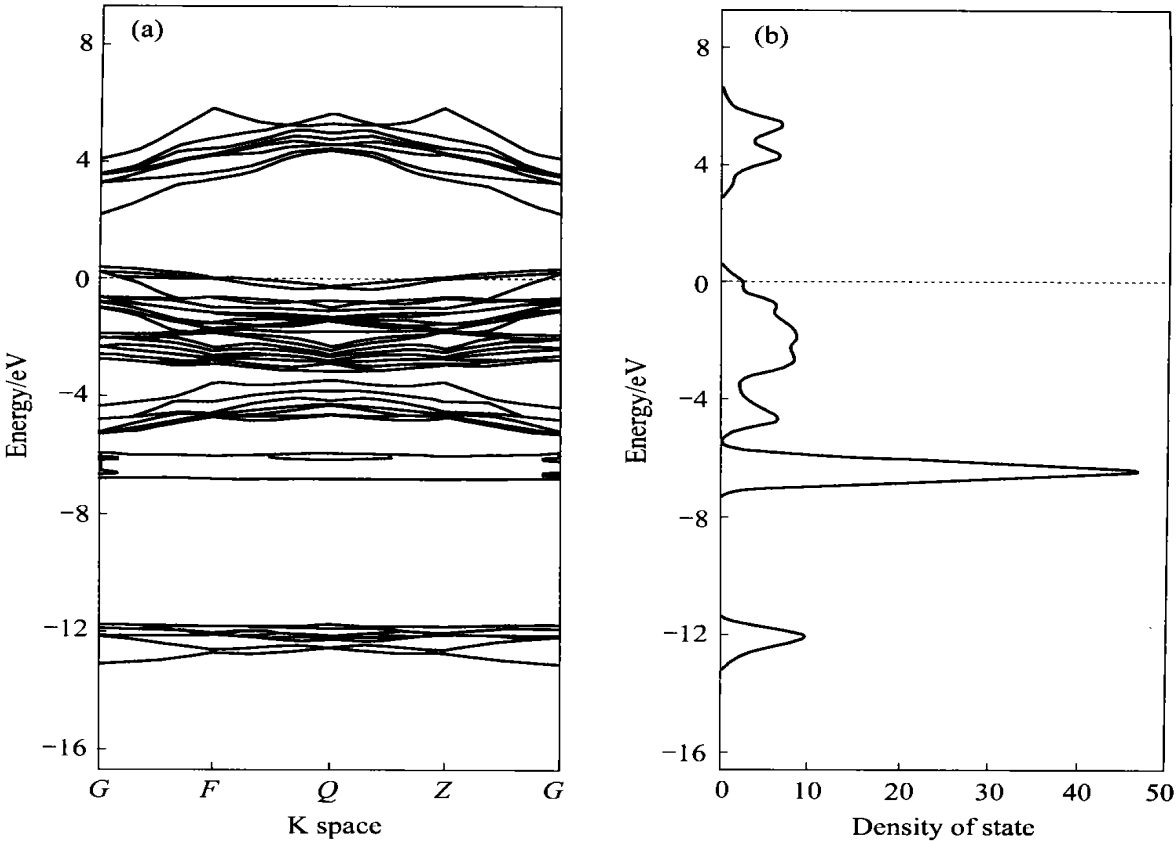**Fig. 5** Calculated partial density of state of elements in marmatite

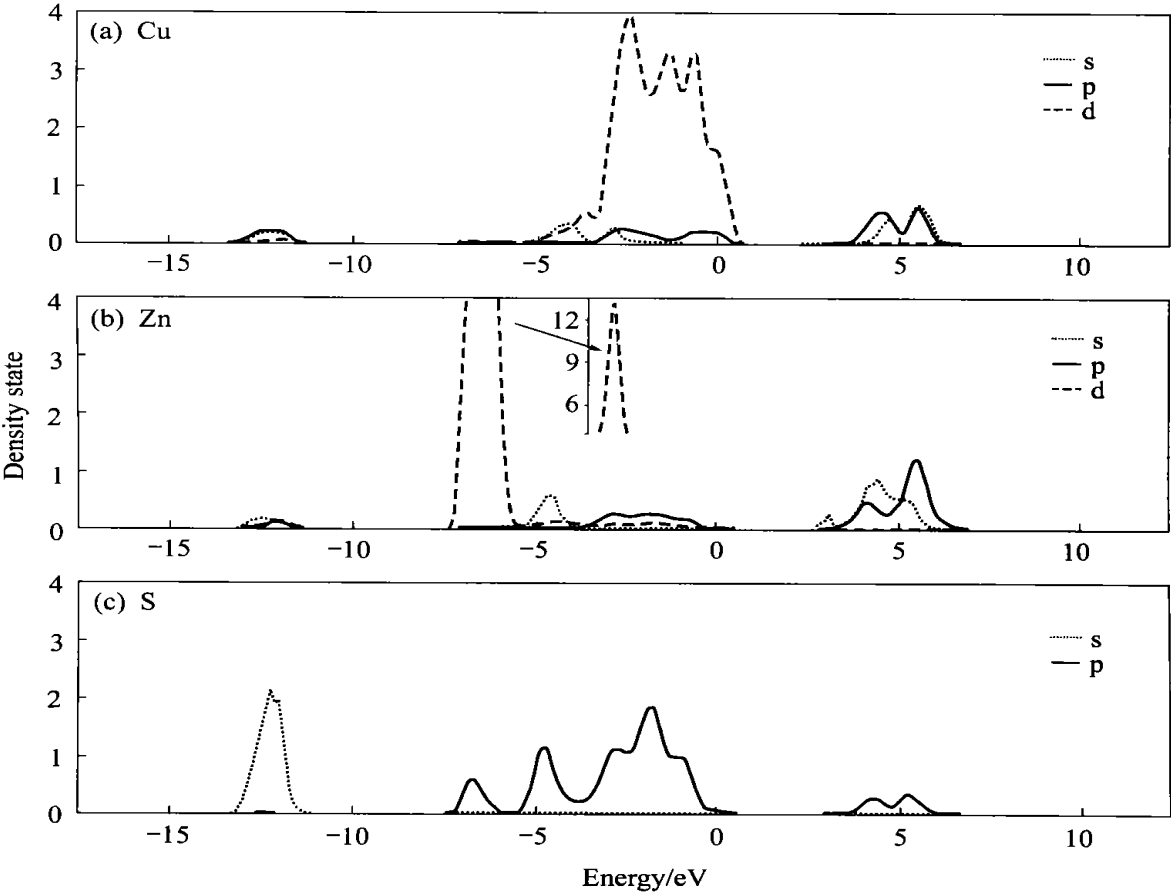**Fig. 6** Calculated band structure(a) and corresponding total density of state(b) of (Zn, Cu)S

Fig. 7 Calculated partial density of state of elements in (Zn, Cu)S

Fig. 5.

4 DISCUSSION

4.1 Effect of doped ions on highest occupied orbit

In the light of mixed potential model[13, 14, 28], it can be concluded that the oxidation of sulfide has a pronounced effect on sulfide mineral flotation. The oxidation will produce metal ions on mineral surface and these ions will react with collectors to render the surface hydrophobicity.

From the DOS patterns shown in Figs. 3, 5 and 7, marmatite and (Zn, Cu)S are the intrinsic semiconductors and sphalerite is a broad band semiconductor. The top valence bands of above three materials are dominantly occupied by Fe 3d, S 3p, and Cu 3d orbits, respectively. According to the frontier orbital theory, the electrons in highest occupied state are most easily bound and have an unexpectedly great significance for the chemical reactivity of materials. It indicates that the different reduction or oxidation will happen on the three mineral surfaces in the pulp during flotation system.

Based on Pattrick's work[29], marmatite is easy to be oxidized than sphalerite and Fe at the (Zn, Fe)S surface. There is also some references to show that the ZnS surface is resistant to oxidation but oxidation of the ZnS surface after Cu activation is apparent[24]. All these studies imply that ZnS has low electrochemistry activity.

ZnS is a broad band semiconductor, and the electrons in the fully occupied valence band are difficult to be excited up to the conduction band. There are less free electrons in ZnS, and then it is not easy to accelerate the electrochemistry oxidation of surface. That is to say, ZnS is difficult to be dissoluted from mineral surface and has little chance to react with thio-collectors. When being substituted by Cu or Fe ions, the forbidden gap of doped ZnS will decrease and the quantity of free electrons in ZnS will increase. This variation will enhance the electrochemistry activity of ZnS.

4.2 Effects of doped ions on mixed potential

Marmatite has a narrower band gap than (Zn, Cu)S does, thus it should be more easily oxidized than (Zn, Cu)S should. But in fact, the sphalerite after Cu activation has the most excellent flotation response using xanthate. These phenomena can be explained by mixed potential theory.

When a system has more than one redox couple, which has different reversible potentials. In such a case, a potential at which the rate of cathodic process of one redox couple will be equal to the rate of anodic process of the other redox couple is measured. Such a potential is located between the reversible potential of the two couples, and so is called "mixed poten-

tial"[30]. This potential also related with electrode material, this to say, different electrode will get different mixed potential from the same solution.

According to the mixed potential theory, an anodic reaction can occur only if there is a cathodic reaction proceeding at finite rate at that potential[31]. For the flotation systems, the cathodic reaction is usually given by the reduction of oxygen:
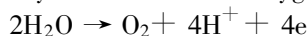
$$2H_2O \rightarrow O_2 + 4H^+ + 4e$$
$$E_r = 1.23 - 0.059pH \qquad (1)$$

The corresponding anodic reaction involves interaction of xanthate on the sulfide minerals in various ways:

1) Reaction of xanthate with the sulfide mineral (MS) to form metal xanthate (MXn):

$$MS + 2X^- \rightarrow MX_2 + S^0 + 2e \qquad (2)$$
$$\text{or} \quad MS + 2X^- + 4H_2O \rightarrow MX_2 + SO_4^{2-} + 8e \qquad (3)$$
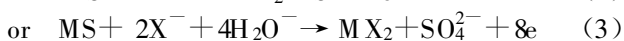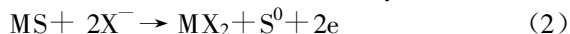
2) Oxidation of xanthate to dixanthogen (X₂) at the mineral surface:

$$2X^- \rightarrow X_2 + 2e \qquad (4)$$

The mixed potential of the sulfide mineral in the flotation pulp will be used to determine the oxidation product on its surface. If the mixed potential of the mineral in the presence of oxygen, xanthate and other reagents is above the mixed potential for X^-/X^2 redox couple, reaction (1) will produce dixanthogen on the surface. If the mixed potential is lower than X^-/X^2 redox couple, reaction (2) will take place and metal xanthate will render the surface hydrophobic.

A lot of works show that the existence of Fe ions on solid surface can catalyze the oxygen reduction. It indicates that the rate of oxygen reduction on marmatite is larger than that on (Zn, Cu)S, which will cause the mixed potential of marmatite to be higher than those of (Zn, Cu)S and ZnS. This process can be illustrated in Fig. 8.

(Zn, FeS) has the highest mixed potential in three kinds of sphalerite. On the marmatite surface, xanthate is easy to be oxidized to dixanthogen
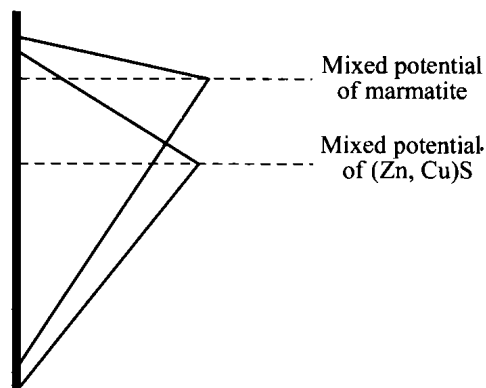

Fig. 8   Schematic of mixed potential of marmatite and (Zn, Cu)S

which is in agreement with QIN's studies[31]. It can explain why $(Zn, Fe)S$ has different floatability compared with $(Zn, Cu)S$.

REFERENCES

[1] Lusk J, Scott S D, Ford C E. Phase relations in the Fe-Zn-S system to 5 kbars and temperatures between 325 and $150 ℃$[J]. Econ Geol, 1993, 88: 1880 −1903.

[2] Pomianowski A, Szczypa J, Poling G W, et al. Influence of iron in sphalerite-marmatite on copper ion activation in flotation[A]. Proc of 11th International Mineral Processing Congress[C]. Cagliari, 1975. 639 −652.

[3] Szczypa J, Komosa S J. A effect of surface oxidation and iron contents on xanthate ions adsorption of synthetic sphalerites[J]. International Journal of Mineral Processing, 1980, 7(2): 151 − 157.

[4] Gigowski B, Vogg A, Wierer K, et al. Effect of Fe-lattice ions on adsorption, electrokinetic, calorimetric and flotation properties of sphalerite[A]. International Journal of Mineral Processing[C]. 1991. 103 − 120.

[5] Finkelstein N P. The activation of sulphide minerals for flotation: a review[J]. International Journal of Mineral Processing, 1997, 52(2 − 3): 81 − 120.

[6] Finkelstein N P. Addendum to the activation of sulphide minerals for flotation: a review[J]. International Journal of Mineral Processing, 1999, 55(4): 283 − 286.

[7] Ralston J, Healy T W. A critation of zinc sulfide with Cu II, Cd II and Pb II — 1. A critation in weakly acidic media[J]. International Journal of Mineral Processing, 1980, 7(3): 175 − 201.

[8] Ralston J, Healy T W. A critation of zinc sulfide with Cu II, Cd II and Pb II — 2. A critation in neutral and weakly alkaline media[J]. International Journal of Mineral Processing, 1980, 7(3): 203 − 217.

[9] Ralston J, Alabaster P, Healy T W. A critation of zinc sulfide with Cu II, Cd II and Pb II — 3. The mass-spectrometric determination of elemental sulphur[J]. International Journal of Mineral Processing, 1981, 7(4): 279 − 310.

[10] Ralston O C, King C R, Tartaron F X. Copper sulfate as flotation activator for sphalerite[J]. Trans AIME, 1930, 87: 389 − 400.

[11] Gaudin A M, Fuerstenau D W, Mao G W. Activation and deactivation studies with copper on sphalerite[J]. Min Eng, 1959, 11: 430 − 436.

[12] Salamy S G, Nixon J C. Recent Developments in Mineral Dressing[M]. IMM, 1953. 503 − 516.

[13] Denzler D, Olschewski M, Sattler K. Luminescence studies of localized gap states in colloidal ZnS nanocrystals[J]. Journal of Applied Physics, 1998, 845 (1): 2841.

[14] Brus L. Quantum crystallites and nonlinear optics[J]. Applied Physics A: Solids and Surfaces, 1991, 53(6): 465 − 474.

[15] QUE W X, ZHOU Y, LAM Y L, et al. Photoluminescence and electroluminescence from copper doped zinc sulphide nanocrystals/polymer composite[J]. Applied Physics Letters, 1998, 73(9): 2727 − 2729.

[16] Bhargava R N, Gallagher D, Welker T. Doped nanocrystals of semiconductors—a new class of luminescent materials[J]. Journal of Luminescence, 1994, 60 − 61: 275 − 280.

[17] Yang P, Lu &die M, Xu &die D, et al. The effect of Co^{2+} and Co^{3+} on photoluminescence characteristics of ZnS nanocrystallines[J]. Journal of Physics and Chemistry of Solids, 2001, 62(6): 1181 − 1184.

[18] Ekwo P I, Okeke C E. Thermoelectric properties of the PbS-ZnS alloy semiconductor and its application to solar energy conversion[J]. Energy Conversion and Management, 1992, 33(3): 159 − 164.

[19] Zunger. Alex stability and electronic structure of ultrafine superlattices and alloys[J]. Acta Polytechnica Scandinavica Electrical Engineering Series, 1987, 58 (8 − 12): 151 − 191.

[20] Edelbro R, Sandstr9 m Ü, Paul J. Full potential calculations on the electron band structures of sphalerite[J]. Pyrite and Chalcopyrite Applied Surface Science, 2003, 206: 300 − 313.

[21] Vaughan D J, Becker U, Wright K. Sulphide mineral surfaces: theory and experiment[J]. International Journal of Mineral Processing, 1997, 51: 1 − 14.

[22] David R. Handbook of Chemistry and Physics, 81rd Edition[M]. Cleveland: CRC Press, 2000. 31.

[23] Jellinek F, Pollak R A, Shafer M W. X-ray photoelectron spectral and electronics structure of zirconium trisulfide and triselenide[J]. Materials Research Bulletin, 1974, 9(6): 845 − 856.

[24] Buckley A N, Woods R, Wouterlood H J. XPS investigation of the surface of natural sphalerites under flotation-related conditions[J]. International Journal of Mineral Processing, 1989, 26(1 − 2): 29 − 49.

[25] Santoni A, Paolucci G, Santoro G, et al. Band structure of lead sulfide[J]. Journal of Physics: Condensed Matter, 1992, 4: 6759 − 6768.

[26] Kashyout A B, Arico A S, Giordano N, et al. Influence of annealing temperature on the crystallographic and optical properties of electrodeposited ZnFeS thin film semiconductors[J]. Mater Chem Phys, 1995, 41: 55 − 60.

[27] Kashyout A B, Arico A S, Monforte G, et al. Electrochemical deposition of ZnFeS thin film semiconductors on tin oxide substrates[J]. Solar Energ Mater Solar Cells, 1995, 37: 43 − 53.

[28] Rand D A J, Woods R. Eh Measurements in sulfide minerals slurries[J]. International Journal of Mineral Processing, 1984, 13(1): 29 − 42.

[29] Pattrick R A D, England K E R, Charnock J M, et al. Copper activation of sphalerite and its reaction with xanthate in relation to flotation: an X-ray absorption spectroscopy (reflection extended X-ray absorption fine structure) investigation[J]. International Journal of Mineral Processing, 1999, 55(4): 247 − 265.

[30] Buckley A N, Woods R, Wouterlood H J. XPS investigation of the surface of natural sphalerites under flotation-related conditions[J]. International Journal of Mineral Processing, 1989, 26(1 − 2): 29 − 49.

[31] QIN Wen-qing. Electrochemistry Mechanic of Sulfide Particle and Potential-control Technique[D]. Central South University of Technology, 1998.

(Edited by YANG Bing)