



A DFT study on the effect of lattice impurities on the electronic structures and floatability of sphalerite

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ABSTRACT

The electronic structures of bulk sphalerite containing 14 typical kinds of impurities were studied by density-functional theory (DFT). The calculated results show that the presence of Cd, Hg, Ga, Ge, In, Ag, Sn, Pb and Sb could increase the lattice parameter of sphalerite. Ag, Sn, Pb, Sb, Cd and Hg impurities narrowed the band-gap and increased the conductivity of sphalerite. Moreover, Mn, Fe, Ga, In, Sn and Sb impurities changed the semiconductor type of sphalerite from p-type to n-type. All of the impurities except Cd and Hg made the Fermi level shift to higher energy and led to the occurrence of an impurity state in the forbidden band.

Analysis of the frontier molecular orbital showed that the impurities Mn, Fe, Cu, Ge, Sn, Pb and Sb contributed greatly to the highest occupied molecular orbital (HOMO) and greatly influence the nucleophilicity of sphalerite. On the other hand, the impurities of Fe, Cu, Co, Ni, Cd and Ga greatly contributed to the lowest unoccupied molecular orbital (LUMO) and greatly affected the electrophilicity of sphalerite. The interactions of O₂ and xanthate with sphalerite are discussed. Results suggest that Mn, Fe, Ni, Cu, Sn and Pb impurities favored the oxidization of sphalerite; however, the impurities of Cd, Hg, Ga and In had the opposite effect. Impurities of Mn, Fe, Co, Ni, Cu, Hg and Pb could enhance the reactivity of xanthate with sphalerite.

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1. Introduction

Sphalerite is an important ore of zinc, and natural sphalerite from different areas usually displays different flotation behaviors. The incorporation of impurities, including iron, cadmium, manganese and copper, are often found in the crystal structure of sphalerite. For example, there are abundant sphalerites with high iron content (up to 8–12%) in Dachang, Guangxi, China (Tong et al., 2006). The sphalerite in Fule, Yunnan province, China is rich in Cd, Se, Ge and Ga, and the Cd content in this region is the highest in China (Si et al., 2006). In Long Lake, Canada, sphalerite ore with Mn, Cd and Hg impurities were also found (Beaudoin, 2000).

Separation of sphalerite from its associated sulfide minerals is commonly carried out by froth flotation, which attaches xanthate to the surface of sphalerite to produce a hydrophobic surface. Generally, the presence of iron decreases the floatability of sphalerite and influences copper activation and the subsequent flotation behavior of sphalerite. However, contradictory results have been reported. Boulton et al. (2005) reported that the presence of iron

in the sphalerite lattice reduced the exchange sites (zinc) for Cu²⁺. On the other hand, XPS analysis showed that the amount of Cu²⁺ adsorbing onto the sphalerite surface increased as the iron content of sphalerite increased (Harmer et al., 2007). In contrast to iron impurity, cadmium (Cd) impurities in the sphalerite lattice improve the floatability of sphalerite. However, there are few reports on the effect of Cd impurity on the flotation behavior of sphalerite.

Lattice defects are known to exert a considerable influence on the properties of minerals (Harmer et al., 2008; Hu et al., 2009). Lattice impurities, for example, can change the electronic properties of sphalerite, including the band-gap, Fermi level, and ratio of free charge carrier concentration. However, systematic knowledge of the correlations between impurities and electronic properties, together with floatability, are lacking for natural sphalerite.

This paper examined fourteen types of impurities, including Mn, Fe, Co, Ni, Cu, Cd, Hg, Ga, Ge, Ag, In, Sn, Pb and Sb, which are all typical substituting impurities in sphalerite (Johan, 1988; Lepetit et al., 2003; Beaudoin, 2000). The aim of the paper is to study the influence of these impurities on the electronic structures and the flotation behavior of sphalerite. This knowledge will provide an understanding of the floatability of natural sphalerite containing impurities.

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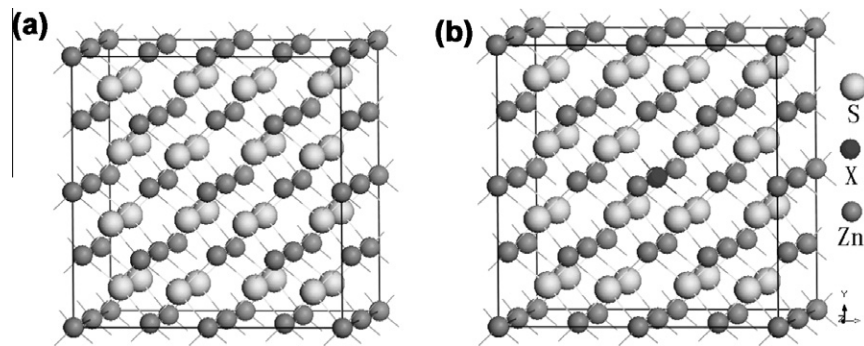


Fig. 1. Supercell of perfect ZnS (a) and impurity-bearing ZnS (b).

2. Computational methods

Geometry optimizations were performed using the Cambridge Serial Total Energy Package (CASTEP), developed by Payne et al. (1992), which is a first-principle pseudopotential method based on density-functional theory (DFT). DFT calculations employing plane wave (PW) basis sets and ultrasoft pseudopotentials were performed (Perdew and Wang, 1992; Vanderbilt, 1990). The exchange correlation functional used was the generalized gradient approximation (GGA) developed by Perdew, Burke and Ernzerhof (PBE) (Perdew et al., 1996). The interactions between valence electrons and the ionic core were represented by ultrasoft pseudopotentials. The kinetic energy cutoff (330 eV) of the plane wave basis was used throughout the study, and the Brillouin zone was sampled with Monkhorst and Pack special k-points of a $2 \times 2 \times 2$ grid for all structure calculations (Monkhorst and Pack, 1976). For self-consistent electronic minimization, the Pulay Density Mixing method was employed. The energy tolerance was 2.0×10^{-6} eV/atom, the force tolerance was 0.05 eV/Å and the displacement tolerance was 0.002 Å. The calculated lattice parameter of perfect ZnS is 0.543 nm, which is very close to the experimental value of 0.541 nm. This value indicates that our calculated results agree well with experimental data.

The atomic orbital coefficient of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and the energies of the frontier orbital of sphalerite were calculated by DMol³ module in Material Studio (Delley, 1990; Delley, 2000) following optimization with CASTEP. The calculations

were performed using GGA–PBE with fine quality, effective core potentials, an atomic orbital basis set of DNP, an SCF density convergence of 1.0×10^{-5} eV and a global cutoff of 4 Å.

Zinc sulfide is naturally observed in two polymorphs, zinc blende and wurtzite, which have cubic and hexagonal lattice structures, respectively (Balaz et al., 1992). The calculation is based on the structure of zinc blende, whose space group is $F-43m$. The unit cell consisted of four zinc atoms and four sulfur atoms, and the cell parameters were $a = b = c = 0.541$ nm and $\alpha = \beta = \gamma = 90^\circ$. A $2 \times 2 \times 2$ supercell was constructed to model bulk ZnS. By replacing one zinc atom by an impurity atom, a model of impurity-bearing ZnS was produced. The models of the supercell are shown in Fig. 1.

The substitution energy of an impurity atom X (Mn, Fe, Co, etc.) for one Zn atom of sphalerite was defined as follows:

Table 1
Substitution energies of impurity atoms substituting for Zn atoms.

Impurity	Substitution energy (eV)	Impurity	Substitution energy (eV)
Mn	−4.49	Ga	−0.08
Fe	−4.60	Ge	−0.68
Co	−3.76	In	0.84
Ni	−3.18	Ag	1.21
Cu	−0.57	Sn	−0.18
Cd	1.42	Pb	−0.10
Hg	3.14	Sb	0.66

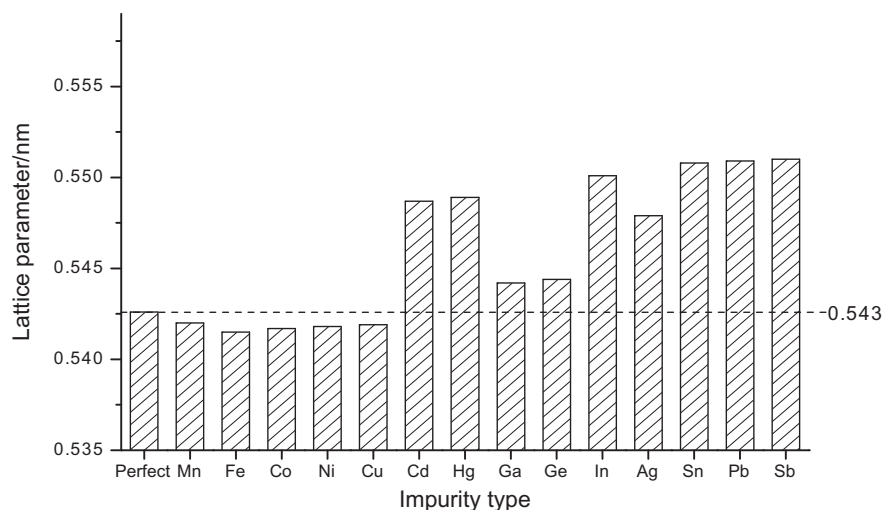


Fig. 2. Lattice parameter of perfect and impurity-bearing ZnS.

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