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Discussion

Structural stability, mechanical properties, electronic structures and thermal properties of XS (X = Ti, V, Cr, Mn, Fe, Co, Ni) binary compounds

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ABSTRACT

The properties of sulfides are important in the design of new iron-steel materials. In this study, first-principles calculations were used to estimate the structural stability, mechanical properties, electronic structures and thermal properties of XS (X = Ti, V, Cr, Mn, Fe, Co, Ni) binary compounds. The results reveal that these XS binary compounds are thermodynamically stable, because their formation enthalpy is negative. The elastic constants, C_{ij}, and moduli (B, G, E) were investigated using stress–strain and Voigt–Reuss–Hill approximation, respectively. The sulfide anisotropy was discussed from an anisotropic index and three-dimensional surface contours. The electronic structures reveal that the bonding characteristics of the XS compounds are a mixture of metallic and covalent bonds. Using a quasi-harmonic Debye approximation, the heat capacity at constant pressure and constant volume was estimated. NiS possesses the largest C_P and C_V of the sulfides.

1. Introduction

Because of the excellent properties of iron-steel materials, they are used extensively in industry. In order to improve the mechanical properties of iron-steel, alloying elements such as Ti, V, Cr, Mn, Fe, Co and Ni are needed. However, sulfur in the material, which is detrimental to the material properties, is usually not eliminated. Sulfides such as TiS and CrS probably exist in the iron-steel. The properties of these sulfides are undefined. In order to design iron-steel materials with outstanding properties, a more comprehensive understanding of the sulfide properties is required.

Researchers have studied the properties of iron-steel experimentally, but the properties of sulfides and the corresponding mechanism are unclear. Accompanied by rapid developments of technology, first-principles calculations [1,2] have been used extensively in material research. Only a few reports exist on experimental studies or theoretical calculations on sulfides. Raybaud et al. [3,4] presented the crystal structures and electronic structures of transition-metal sulfides. In the local density approximation, a pronounced trend exists towards an overbinding, which manifests itself in the prediction of undersized atomic volumes and oversized cohesive energies. The local density approximation and the generalized gradient approximation are accurate to establish correlations with the catalytic activities of transition-metal sulfides. Franzen et al. [5] estimated the thermodynamic properties of titanium monosulfide. The vaporization of stoichiometric TiS has been shown to be congruent, and the products are TiS molecules and probably Ti and S atoms. Bridgeman et al. [6] studied the bond lengths and electronic structures of TiS and VS. Han et al. [7] synthesized a NiS phase using mechanical alloying (MA). Kavcl et al. [8] investigated the stability and dynamic properties of MnS. The authors found α-MnS to be the most stable phase, and stiffer than others, whereas γ-MnS is the highest compressible material. β- and γ-MnS crystals show covalent characteristics.

To the best of our knowledge, the elastic coefficients, elastic moduli, electronic structures and thermal properties of XS (X = Ti, V, Cr, Mn, Fe, Co, Ni) binary compounds are seldom discussed systematically as a group. However, research on the properties of sulfides is helpful for further research on iron-steel materials. Therefore, the mechanical properties, electronic structures and thermal properties of sulfides using first-principles calculations within the GGA (generalized gradient approximation) formalism have been investigated systematically using these sulfides as a group in this study.

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2. Methods and details

First-principles calculations were used to estimate the elastic constants and moduli, electronic structures and thermal properties of XS (X = Ti, V, Cr, Mn, Fe, Co, Ni) binary compounds, as performed in the Cambridge Serial Total Energy Package (CASTEP) code [9]. Ultrasoft pseudopotentials were used to describe the interactions between valence electrons and pseudo-ion cores [10]. The valence electrons of Ti, V, Cr, Mn, Fe, Co, Ni and S are $3s^23p^63d^24s^2$, $3s^23p^63d^34s^2$, $3s^23p^63d^54s^1$, $3s^23p^63d^54s^2$, $3s^23p^63d^64s^2$, $3s^23p^63d^74s^2$, $3s^23p^63d^84s^2$ and $3s^23p^4$, respectively. The Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional of the generalized gradient approximation (GGA) was used [11]. In order to achieve equilibrium crystal structures of these sulfides, the BFGS (Broyden–Fletcher–Goldfarb–Shannon) algorithm was used [12]. In this study, spin polarized calculations were conducted. The self-consistent total energy is at 1×10^{-9} eV, and the maximum force on the atom was below 0.01 eV/Å. The Pulay density mixing scheme was used in the electron energy minimization. A plane-wave expansion with 450 eV kinetic energy cut-off energy was applied. The Monkhorst–Pack scheme [13] was used for k-point sampling in the first irreducible Brillouin zone (BZ), as $10 \times 10 \times 8$ for the calculation of structural stability, elastic constants and electronic properties for all compounds.

In this study, two parameters were used to estimate the thermodynamic stability of the sulfides with the following equations [14–17]:

$$E_{coh}(X_aS_b) = \frac{E_{total}(X_aS_b) - aE_{iso}(X) - bE_{iso}(S)}{a+b}, \quad (1)$$

$$\Delta_r H_m(X_aS_b) = \frac{E_{total}(X_aS_b) - aE_{bulk}(X) - bE_{bulk}(S)}{a+b}, \quad (2)$$

where $E_{coh}(X_aS_b)$ and $\Delta_r H_m(X_aS_b)$ are the cohesive energy and formation enthalpy, respectively. $E_{iso}(X)$ and $E_{iso}(S)$ are the total energy of an isolated X and S atom, respectively. $E_{total}(X_aS_b)$ is the total compound energy. $E_{bulk}(X)$ and $E_{bulk}(S)$ are the chemical potential of X and S atoms in the bulk state, respectively. The elastic constants were achieved using the stress–strain method in an equilibrium structure [18]. The detailed calculation procedure for the elastic constants is similar to our previous paper [19].

The elastic moduli of the sulfides, such as the bulk modulus (B), shear modulus (G), Young's modulus (E) and Poisson's ratio (σ), were achieved using the Voigt–Reuss–Hill approximation. The formulae are given by [20]:

$$B_{VRH} = \frac{1}{2}(B_V + B_R), \quad (3)$$

$$G_{VRH} = \frac{1}{2}(G_V + G_R), \quad (4)$$

$$E = \frac{9B_{VRH}G_{VRH}}{3B_{VRH} + G_{VRH}}, \quad (5)$$

$$\sigma = \frac{3B_{VRH} - 2G_{VRH}}{2(3B_{VRH} + G_{VRH})}, \quad (6)$$

where B_V/G_V, B_R/G_R and B_{VRH}/G_{VRH} are the bulk modulus/shear modulus that is estimated using the Voigt, Reuss and Voigt–Reuss–Hill approximation methods, respectively.

3. Results and discussions

3.1. Stability

The crystal structures of the sulfides are presented in Fig. 1. The cohesive energy and formation enthalpy are used to achieve a thermodynamically stability of XS (X = Ti, V, Cr, Mn, Fe, Co, Ni) binary compounds, as depicted in Table 1. The error between our results and other experimental data [3,8,21–27] is less than 5%. This situation may be caused by the influences of experimental equipment and different calculation methods. Therefore, our adopted parameters are reliable in this research. The cohesive energy and formation enthalpy show the stability of the combination of two atoms, and the stability of the formation of compounds, respectively [17]. Because the two parameters are negative, these sulfides are thermodynamically stable. With an increase in ionic radius of X, the cohesive energy of the XS binary compounds increases initially, and then decreases. The minimum cohesive energy and formation enthalpy are attributed to CrS and TiS. According to the theory of the lowest energy, CrS has a stronger stability for the combination of two atoms among the XS binary compounds, and TiS may be the most stable compound among the sulfides. Fig. 2 depicts the formation enthalpy of sulfides as a function of the ionic radius of X. Because no experimental data exist to contradict our results, they can be used only as a guideline.

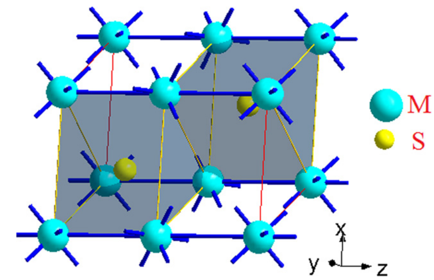

Fig. 1. The crystal structures of the XS (X = Ti, V, Cr, Mn, Fe, Co and Ni) binary compounds.

Table 1
The calculated lattice parameters (a, b, c in Å), cohesive energy (eV/atom) and formation enthalpy (eV/atom) of XS (X = Ti, V, Cr, Mn, Fe, Co, Ni) binary compounds.

Species	$a = b$	c	Cohesive energy	Formation enthalpy
TiS	3.334 (3.296[a], 3.305[b])	6.349 (6.398[a], 6.342[b])	−6.73	−1.21
VS	3.189 (3.340[c])	6.259 (5.785[c])	−6.93	−0.53
CrS	3.172 (3.439[c])	5.805 (5.324[c])	−7.47	−0.35
MnS	3.489 (3.81[d])	6.053 (6.77[d])	−6.90	−0.19
FeS	3.311 (3.674[e])	5.046 (5.033[e])	−7.09	−0.59
CoS	3.354 (3.37[f], 3.367[g])	5.177 (5.16[f], 5.16[g])	−6.53	−0.41
NiS	3.469 (3.435[h], 3.448[i])	5.203 (5.344[h], 5.359[i])	−5.96	−0.29

[a] Exp. in Ref. [21].
[b] Exp. in Ref. [22].
[c] Exp. in Ref. [3].
[d] Cal. in Ref. [8].
[e] Exp. in Ref. [23].
[f] Exp. in Ref. [24].
[g] Exp. in Ref. [25].
[h] Exp. in Ref. [26].
[i] Exp. in Ref. [27].

3.2. Mechanical properties

Fig. 3 shows the relative volume V/V_0 and bond length ratio of the sulfides as a function of pressure. The relative volume is defined as the volume anticompressibility, which decreases with an increase in pressure, as shown in Fig. 3(a). From Fig. 3(a), the highest volume anticompressibility belongs to CrS, because it has