From predicting to correlating the bonding properties of iron sulfide phases

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\textbf{A B S T R A C T}

Iron sulfides have emerged as a fascinating class of materials in electromagnetics and catalysis areas, which however are challenging in first-principles modeling because of the strongly-correlated interactions between Fe 3d and S 3p electrons. Here, we assess the performances of 14 density functionals on the structural, electronic, and magnetic properties of five iron sulfides. The PBE + U with \( U = 2.0 \) eV has the overall best performance. After evaluating functionals and obtaining reliable properties, our final goal is from predicting to correlating in order to do high throughput screening for the systems since the complex structures and phases of iron sulfides, to put it in another way, to hunting a reliable descriptor for predicting their properties. In the work, we demonstrate that the crystal orbital Hamilton population (COHP) and Bader charge of Fe atoms presents a good correlation with the empirical bond valence. Our results open a new avenue to effectively investigate phases and properties for various structures of iron sulfides. Indeed, the correlations between COHP/Bader charge and bond valence can be extended to other systems.

1. Introduction

Metal sulfide minerals play a significant role in industrial and economic society since many metals such as zinc, copper, lead, gold, and platinum are derived from sulfides ores. Among them, iron sulfides are the most widely investigated due to their extensive distribution in the earth. They usually exhibit a wide range of physical, electronic and chemical properties which make it possible for applications in solar cells, electromagnetic devices and electro- and photo-catalysts \cite{1–3}.

Under certain temperature and pressure, iron sulfides compounds can undergo a variety of forms by changing the stoichiometries that range from the sulfur deficient mackinawite FeS\textsubscript{1−x} through iron-deficient pyrrhotites Fe\textsubscript{1−x}S to pyrite FeS\textsubscript{2} \cite{4}. Their abundant structures bring much difficulty for experimental characterizations. With the development of density functional theory (DFT), the theoretical calculation has become an effective “characterization tool” in physics, chemistry, and material sciences. However, the DFT calculations are very computationally expensive. Therefore, it is of great significance and desirable to develop an effective method or model to describe the complicated chemical environment of Fe atoms in Fe-S compounds for the investigation of the intrinsic properties of iron sulfides systems. One of the most challenge task in DFT calculations is the modeling of strongly-correlated interactions between Fe 3d electrons, which is a key to predict the structural and electronic properties of ground states. Joseph et al. \cite{5} studied the structural parameters and the band gap of pyrite FeS\textsubscript{2} utilizing Local Density Approximation (LDA) \cite{6}, the lattice constants were \( a = b = c = 5.386 \) Å, which are less than experimental value of 5.418 Å. As for the fundamental band gap, LDA predicted pyrite as metal while the real gap is 0.95 eV by the experimental photoelectron spectrum. The LDA functional which is based on the homogeneous electron gas model underestimates the structural parameters and band gaps, especially for strongly-correlated systems. Generalized Gradient Approximation (GGA, Perdew, 1996) \cite{7} have provided a practical method to successfully explore the structural and electronic properties of ground states across the periodical table. Spagnoli et al. \cite{4} used GGA-PBE and PBEsol \cite{8} approximation and present a study on structural properties of polymorphs pyrite and marcasite, the calculation results reveal that GGA could give much better lattice constants.

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respect to LDA. Whilst the band gap of pyrite is also predicted to be 0 eV, suggesting that GGA also fail to capture the electronic structure of the ground state.

An effective method to treat with the strongly-correlated system is to add a Hubbard parameter, localized term, to LDA or GGA density functional, also known as DFT + U approximation [9,10]. Choi et al. [11] reported that the predicted band gap of pyrite is 1.03 eV with GGA + U where Ueff is equal to 2.0 eV, which is very close to an experimental gap of 0.95 eV. Koutti et al. [12] employed spin polarization LSDA + U approximation to investigate the magnetic property and band gap of troilite FeS, the effect of Ueff on results are also taken into account. They found that with the increasing of Ueff, the magnetic moment and band gap is increasing. When Ueff = 2.0 eV, the magnetic moment is 3.66 μB and the band gap is 0.54 eV, these results are well in accordance with experimental observation of 3.50 μB and 0.50 eV. Another route to address strongly-correlated materials is hybrid functional, such as B3LYP [13], PBE0 [14], and HSE [15]. In hybrid DFT, the self-interaction error of conventional DFT is partially corrected by embedding a fixed part of exact, nonlocal Hartree-Fock (HF) exchange into exchange-correlation functional.

To have a brief view of the performances of different density functional approximations on describing bulk properties of iron sulfides, we summarize previously reported studies as shown in Table 1. Just as we know, the rational calculation method is the basis for further our calculations.

![Table 1](image)

### Table 1

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2. Theoretical methods and computational details

To characterize magnetism, all calculations are carried out within the framework of the spin-polarized density functional theory using the projected augmented wave (PAW) method [27], as implemented in the Vienna Ab Initio Simulation Package (VASP) [28]. The Brillouin zone is sampled using Monkhorst-Pack generated a set of k-mesh, 6 × 6 × 6 for pyrite, 7 × 6 × 9 for marcasite and 7 × 7 × 5 for mackinawite, 11 × 11 × 6 for NiAs-troilite and 6 × 6 × 3 for troilite, all the k-points are centered with Gamma point. The plane cutoff of the energy of 500 eV is used to describe the electronic wave-function. All the atoms are relaxed to their equilibrium positions when the change in energy on each atom between successive steps is converged to 1.0 × 10⁻⁵ eV/atom, the forces on each atom are converged to 0.02 eV/Å.

In our calculations, Hartree-Fock [29,30], local density approximation (LDA) [31], generalized gradient approximations (GGA-PBE and GGA-PBEsol) [6], meta-GGA (TPSS and SCAN) [32], Hubbard U model (DFT + U approach) and hybrid functionals (B3LYP, PBE0, and HSE) are used. For the GGA + U approach, in the formulation of Lichtenstein [9] and later Dudarev [10], where only a single parameter, Ueff, determines an orbital-dependent correction to the GGA calculation energy. Here, the Ueff is equal to 2.0, 2.5, 3.5 and 4.5 eV, respectively.

In the HSE approach, the exchange–correlation part is shown in Eq. (1), where α = 0.08, 0.10, 0.15, 0.20 and 0.25, ω = 0.207 is used in our calculations.

\[ E_{\text{HSE}} = \alpha E_{\text{HF,SR}} (\omega) + (1 - \alpha) E_{\text{PBE,SR}} (\omega) + E_{\text{PBE,LR}} (\omega) + E_{\text{PBE}} \]  

(1)

3. Results and discussions

3.1. Iron sulfides structures

Iron and sulfur could form various structures and phases under specific conditions. In this work, we focus on only five representative iron sulfides including two FeS₂ phases (pyrite and marcasite) and three FeS phases (mackinawite, troilite, and NiAs-troilite), the crystal
structures are presented in Fig. 1. The unit cell of pyrite FeS₂ is simple cubic with Pa₃ space group containing 4 iron atoms and 8 sulfur atoms, as shown in Fig. 1(a). The structure of pyrite is similar to NaCl crystal with the Fe ion occupying the Na position and the S dimer locates at the Cl ion position. Each Fe atom is octahedrally coordinated with surrounding six S atoms where each S atom bond to three Fe atoms and one S atom. The lattice parameter is \( a = b = c = 5.418 \) Å with experimental characterization. Pyrite is a promising photovoltaic material with a suitable band gap of 0.95 eV in experiment [21].

Marcasite FeS₂ is a polymorph of pyrite that attributes to \( \text{Pnma} \) space group and crystallizes in orthorhombic. Just as shown in Fig. 1(b), each Fe atoms is coordinated with surrounding four sulfur atoms while each S atoms bond with three nearby S atoms and one Fe atom. At low temperatures, the marcasite is metastable phase respect to pyrite, but it can transform to pyrite when the temperature is around 700 K [33]. Compared to pyrite, the corresponding studies no matter experimental or theoretical studied on marcasite are much less. The experimental lattice constants of marcasite are \( a = 4.440, b = 5.432 \) and \( c = 3.386 \) Å. Jagadeesh and Seehra found that the band gap of marcasite is 0.34 eV [34], but later research has proved that the band gap of marcasite is no lower than pyrite and maybe larger than 0.95 eV [35].

The layer-type mackinawite is modeled in the tetragonal structure (Fig. 1(c)). Both room temperature neutron diffraction [36] and Mossbauer data at 4.2 K [24] testify the absence of magnetic moment in mackinawite. The lattice parameter is \( a = b = 3.674 \) and \( c = 5.033 \) Å measured experimentally [6]. Vaughan and Ridout [24] have demonstrated that the mackinawite presents a metallic character with the electronic states of Fe d-orbitals dominating the regions around the Fermi level. According to the previous study, at ambient pressure and room temperature stoichiometric FeS crystallizes in the troilite structure with a hexagonal space group \( \text{p6} \text{mc} \), as shown in Fig. 1(e). At high temperature, the Fe ions would be shifted away from their ideal positions and transformed to high symmetry hexagonal \( \text{p} \text{6}_{3} \text{mc} \) space group, the so-called NiAs-type structure (Fig. 1(d)). Below \( T_{\text{m}} \sim 588 \) K, FeS undergoes an antiferromagnetic (AFM) phase with a narrow band gap, while a high temperature, FeS behaves as a metal [3].

### 3.2. XC-functionals performance for iron sulfides

We first investigate the lattice constant of five iron sulfides with different functionals, the results are summarized in Table S1. The experimental constants, mean absolute error (MAR) and the mean absolute relative error of calculated lattice constants (MARE, %) are also provided to compare with each other. For pyrite and marcasite, the MAR and MARE of these functionals are all within 0.1 Å and 2%, respectively. It means that the structural predictions of FeS₂ are independent of density functional approximations. Whilst for mackinawite, GGA-PBEsol, meta-GGA (SCAN) and PBE + U (\( U_{\text{eff}} = 2.0 \) eV) could give reasonable lattice constant when compared to experimental values, the MARE are all within 2%, but for other functionals, the MARE is beyond 4%. From Table S1, functionals (PBE, TPSS, PBE + U (\( U_{\text{eff}} = 2.5, 3.5 \) and 4.5)) overestimate the lattice constant in c direction. Dzade et al. [6] investigated the bulk property and water adsorption on surfaces of mackinawite with DFT-D2 approximation, the results show that the structural parameters are consistent well with experimental values when van der Waals interaction is considered. For NiAs-type troilite, only the lattice constant predicted with PBE + U (\( U_{\text{eff}} = 2.0/2.5 \) eV) is well consistent with experimental data, the MARE of calculated lattice constant is within about 2%. For troilite, only PBE + U (\( U_{\text{eff}} = 2.0 \) eV) could give accurate structure parameters.

To have a clear overview of the performance of the different functionals in predicting iron sulfides structural property, we plot the relative error (%) of predicted lattice constants in Fig. 2. It can be found that LDA, PBEsol, and SCAN underestimate the lattice constant for all these five iron sulfides. PBE and TPSS overestimate the lattice constant for mackinawite while underestimated for other four sulfides. PBE + U (\( U_{\text{eff}} = 2.5/3.5/4.5 \) eV) overestimate the lattice parameters for these sulfides, and with the increasing of \( U_{\text{eff}} \) the MARE is also increasing. From above-computed results, we tentatively conclude that PBE + U with \( U_{\text{eff}} = 2.0 \) eV could give accuracy lattice constants for iron sulfides.

One of the important applications of iron sulfides is that they can serve as electromagnetic devices. Therefore, it is of significance to investigate their magnetic and electronic properties. We calculated the magnetic orderings, magnetic moments and fundamental band gaps of these five iron sulfides. Table S2 summarizes the results with the different functionals.
various XC-functionals. Except for functionals used in structural prediction, we further select Hartree-Fock and hybrid functional (B3LYP, PBE0, and HSE06) to perform a static self-consistent convergence calculation based on optimized structures with PBE + U (U\text{eff} = 2.0 eV). Many studies have reported that hybrid functional could be good at describing the magnetic property and fundamental band gaps respect to experimental observations, especially for strongly-correlated systems such as transition metal oxides [37–39]. From Table S2, all these functionals used in this work predict polymorphs FeS\textsubscript{2} (pyrite and marcasite) as nonmagnetic (NM) material, this is in coincidence with experimental observations [18]. For three FeS cases, because the magnetic orderings are more complex than FeS\textsubscript{2}, we first calculated the relative energies (eV/unit) for antiferromagnetic (AFM), ferromagnetic (FM), and non-magnetic (NM) states with different functionals as shown in Table S3. Only the most stable states are summarized in Table S2. For mackinawite, LDA, GGA, and meta-GGA all give the predictions that non-magnetic states are more stable in energy, which is in line with experimental results. As PBE + U, when U\text{eff} = 2.0 and 2.5 eV, the mackinawite is predicted to be non-magnetic, when U\text{eff} is beyond 2.5 eV, the AFM state becomes more stable. In layer-type mackinawite, the adsorb-like sulfur atoms are located at hole site of quadrilateral four Fe atoms, the hybridization between Fe 3d states and S 3p states is obviously overestimated, the trend is in line with the study on the magnetic moment as described above. While for marcasite, the results are not the same. LDA, GGA, meta-GGA (SCAN) and PBE + U (U\text{eff} = 2.0 eV) could give reasonable band gaps. TPSS and HF give a zero band gap, other approaches all overestimated the band gaps. What’s more, it’s interesting to note that all these functionals predict mackinawite as conductor except for PBE + U (U\text{eff} = 4.5 eV). For NiAs-troilite, PBE + U when U\text{eff} is beyond 2.0 eV and HF give inaccurate band gap while other approaches are qualified in describing the band gap. Go so far as to troilite, the experimental band gap is around 0.5 eV. However, in the above-involved approximations, only predictions of PBE + U with U\text{eff} = 2.0 eV and HSE06 with 15% Hartree-Fock are comparatively reasonable.

For the sake of providing a succinct and clear profile about different functionals compartment in describing the magnetic and electronic properties of iron sulfides, we compare the deviation between calculation and experiment as plotted in Fig. 3. If the symbols fall on black solid lines, it indicates that the predicted results are in coincident with experimental values. It can be perceived from Fig. 3(a) that LDA, PBE, and TPSS all underestimate magnetic moments for troilite, B3LYP, PBE0, as well as HSE06, overestimate moments for mackinawite. In brief, PBE + U (U\text{eff} = 2.0 eV) is an excellent choice to forecast the magnetic property of iron sulfides. In pyrite case, LDA and GGA underestimate the band gaps (0.5 eV vs 0.98 eV). Two meta-GGA functional predict it to be a metal other than a semiconductor. The band gap with PBE + U where U\text{eff} = 2.0 eV is 0.94 eV, in excellent agreement with the experiment of 0.95 eV. To continue to increase effective Hubbard U, the band gap is broadened step by step which is in agreement with our previous study on transition metal oxides [42].

Fig. 3. (a) The calculated magnetic moment (μ\textsubscript{B}) and (b) band gap (eV) with different DFT approximations (horizontal axis present experimental data, vertical axis are calculated values).
approximate to experimental values.

According to our above systematic studies, we can tentatively draw a conclusion that PBE + U with U_{eff} = 2.0 eV could be qualified in predicting the structural parameters, magnetic moments and band gaps for iron sulfides. Thereafter, we explore the Density of States (DOS) for involved five iron sulfides utilizing Hubbard U approximation where U_{eff} is equal to 2.0 eV and then compare the DOS with experimental photo-electronic spectrum. The conceptually most straightforward method to get band gaps is from direct and inverse X-ray photoelectron spectra (XPS and BIS) or X-ray emission and absorption spectra (XES and XAS).

In Fig. 4, one can well perceive that the peak positions of valence and conduction bands by theoretical calculations are highly consistent with experimental spectrum, this confirms that Hubbard U with U_{eff} = 2.0 eV is good in predicting the electronic properties of iron sulfides. As regards the DOS by other approximations, the detailed results are plotted in Figs. S1–S5.

3.3. Electronic structure of iron sulfides

After the scientific benchmark of different calculation methods, we intend to discuss the electronic band structure and bonding property for these five iron sulfides. The electronic band structure and corresponding local density of states (LDOS) of these iron sulfides compounds are calculated utilizing PBE + U with U_{eff} = 2.0 eV as displayed in Fig. 5. Here the DOS is decomposed into the most significant bonding contributions in the energy range around the Fermi level, which are S 3p and Fe 3d orbital contributions. For iron sulfide pyrite, Fig. 5(a), it’s not difficult to detect an indirect band gap of 0.95 eV. The valence band maximum is located between M and G K-points while the conduction band minimum is located at G K-point. From the LDOS, the most contributions between −4 eV to 4 eV are Fe 3d states with a non-neglected S 3p states, it signifies that in this energy range the hybrid of Fe 3d and S 3p is strong. The covalent bond of the S dimers contributed to S 3s and S 3p orbitals are located at lower energy range which is not presented here.

The FeS₂ marcasite is structurally closed to iron pyrite and is confirmed that can co-exist with pyrite under certain conditions. From Fig. 5(b), one can find that marcasite has a similar band gap to pyrite, which is about 1.0 eV as corresponding to 0.95 eV for pyrite. In 1980, the optical band gap of marcasite has been reported to be 0.34 eV characterized by electrical resistivity measurements [34], which far deviates from recent experimental studies and DFT calculations. The reason might be that the stoichiometric composition is quite difficult to control in experimental conditions, the S atoms are too easily escape from the solid surface to reproduce sulfur vacancies. The band gap is drastically decreased when a sulfur vacancy appears. Based on our calculations, marcasite also exhibits an indirect band gap where the valence band maximum is located at \( \Gamma \) high-symmetry K-point while the conduction band minimum is located at U K-point.

For tetragonal FeS, namely mackinawite, from our calculated density of states and electronic band structure as shown in Fig. 5(c), one can find that the Fermi level cuts a band of Fe 3d orbital, indicating the presence of mobile electrons carriers with metallic nature which is...
concordant with previous DFT and experimental studies [6]. When compared to above two FeS2 cases, the dominant contribution near the Fermi energy level is deriving from Fe 3d states, the primary interactions are coming from the direct intralayer Fe-Fe bonds, the calculation result is well consistent with the general DOS features of layer-type tetragonal iron-based compounds [43].

The iron mono-sulfide troilite transfers to NiAs-troilite when the temperature is above the Neel temperature of 588 K. Next, we study the change of electronic structures of FeS below and above Neel temperature. Below Neel temperature, the FeS crystallizes in troilite structure with antiferromagnetic orderings, previous literature has reported that troilite appeared to be a semiconductor with a much-narrowed band gap of 0.04 eV whereas behaves like metal when above Neel temperature [26]. But latter photoemission and bremsstrahlung isochromat spectroscopy (BIS) spectra revealed that the real band gap of FeS should be larger than 0.04 eV whereas behaves like metal when above Neel temperature [26]. However, our calculations are consistent with these experiments.

Moreover, in two FeS2 cases, the contributions of S 3p should not be ignored no matter in valence or conduction bands below and above the Fermi level, this indicates that pyrite and marcasite should fall in the realm of charge transfer insulators. While for troilite, the bands near the Fermi level are dominated by Fe 3d states, suggesting that it belongs to Mott-Hubbard insulator.

3.4. Bonding analysis

After evaluating XC-functionals and obtaining reliable data of properties, one can have a large space to play in predicting and correlating something. As known, the crystal structures and phases are very complicated for iron sulfides for its polymorphs. As a result, numerous non-stoichiometric phases make a great challenge to investigate their properties. The intrinsic difference is the various coordinated conditions for centered Fe atoms. The routine way to capture the properties of these phases is to the brute-force calculations carried out one by one, which is however infeasible because the calculations are much computational expensive. Therefore, it is critical to developing a model to describe the bonding character of Fe-S in different crystal, and a relationship between bonding character and other properties. To put it in another way, from a big data point of view, one can use a simple model or calculations to predict/calibrate more properties for various structures. Here, based on PBE + U (U_{eff} = 2.0 eV) static self-consistent calculations, the Crystal Orbital Hamilton Population (COHP) analysis of Fe-S bonds has been performed. This COHP approach is analogous to the Crystal Orbital Overlap Population (COOP) developed by Hoffmann in the context of extended Hückel calculations [45,46]. The purpose of COOP (COHP) is to extract the information of chemical bonding out of the standard DFT calculations, the positive and negative values of COOP present bonding and anti-bonding, respectively. For COHP, the meaning is just the opposite. If the COOP or COHP is zero, it suggests a non-bonding interaction.

We extract the chemical bonds with a centered Fe and plotted the total COHP in Fig. 6. The orange filled area presents Fe-S bonding, while the green filled area presents Fe-S anti-bonding. In Fig. 6(a)–(c),
one can see that when the energy level is below $-1$ eV, there is mainly bonding contribution, whereas from $-1$ eV to the maximum occupation energy level, namely the Fermi level, there is only anti-bonding distribution. This indicates that the Fe atoms in these three sulfides are binding strongly with coordinated S atoms, also suggests these phases are stable. While for polymorphs NiAs-troilite (Fig. 6(d)) and troilite (Fig. 6(e)), the anti-bonding region are extended from Fermi level to $-5$ eV, this occupied anti-bonding weaken the interactions between Fe-S.

Bond valence model derived from Pauling’s rule is a robust method to validate the chemical structure and evaluate the oxidation states of atoms, even be used to predict other properties of complex structures. Steinfink et al. have proposed a model to describe the relationship between bond valence and bond length for iron-sulfur compounds [47]. The empirical bond valence is calculated based on Eq. (2)

$$V = S_0 \sum_{i=1}^{CN} (R_i/R_0)^{-n}$$

(2)

where $V$ is the valence, $R_i$ is the bond distance, and $CN$ is the coordination number. The constants $S_0$ is chosen as $1/3$, the $R_0$ is a hypothetical value for Fe$^{2+}$ in an octahedral environment. The resultant equation for the iron-sulfur compounds is

$$V = 1/3 \sum_{i=1}^{CN} (R_i/2.515)^{-6.81}$$

(3)

The bond valence could reflect the bond strength, the integrated COHP (ICOHP) could also give the information of strength for the specific bond. If the empirical model is rational, the bond valence should have a liner relationship with the ICOHP. We calculate the ICOHP for centered Fe atoms in five iron sulfides as presented in Table 2. The ICOHP of Fe atoms in polymorphs FeS$_2$ marcasite and pyrite is larger than that of in other phases, indicating that the Fe interacts strongly with surrounded S atoms in these two polymorphs. While in two troilite phases, the ICOHP is small, suggesting that the weak bonding for centered Fe atoms. This is well consistent with the above COHP analysis. The ICOHP as a function of bond valence is plotted in Fig. 7(a), indicating that the ICOHP presents a good liner relation with Fe bond valence. This correlation suggests that the empirical bond valence model is reasonable to describe the character of iron-sulfur bonds in order to predict the stability of iron-sulfur phases.

Furthermore, we have calculated the Bader charge of centered Fe atoms in different phases (Table 2) and establish the correlation between Bader charge and Fe-S bond valence, as shown in Fig. 7(b). The Bader charge is a liner function of bond valence. Because the charge of atoms is re-distributed after bonding, the charge gathering or deletion is a signal for bonding strength. Our result indicates that this empirical bond valence model could extend to other iron sulfides phases and explore their properties. We know that the bonding stability or charge character are important factors in screening and designing functional and catalytic materials. In this way, such correlations can save the expensive computation resources in DFT, and achieve fast-speed predictions.

4. Conclusions

We assess the performance of 14 XC-functional of DFT including HF, LDA, GGA, meta-GGA, DFT + U as well as hybrid functional on structural, magnetic and electronic properties of two FeS$_2$ and three FeS polymorphs. The calculation results reveal that PBE + U with $U_{eff} = 2.0$ eV could give reasonable predictions for lattice constants, magnetic orderings and moments as well as fundamental band gaps. Using PBE + U ($U_{eff} = 2.0$ eV) calculations, FeS$_2$ polymorphs pyrite and marcasite both show non-magnetic, and get 0.94 eV and 0.98 eV indirect band gaps, respectively. The electronic band structures indicate they are charge transfer semiconductors. For three FeS polymorphs, mackinawite with layer-type structure is a non-magnetic and metallic material. While troilite and NiAs-troilite, they both present AFM orderings and the band gaps are 0.64 eV and 0 eV for troilite and NiAs-troilite, respectively. At last, the COHP, as well as Bader charge of centered Fe atoms in various sulfides is calculated. We find that the ICOHP and Bader charge has a good liner relation with bond valence from the empirical model. Our model could open a new routine to effectively study the bonding characters and other properties for various iron sulfides phases and structures. The correlations between bonding and electronic property will help us to achieve fast-speed predictions of properties and high throughput screening of interesting phases for further applications.

Table 2

<table>
<thead>
<tr>
<th>FeS$_2$ (pyrite)</th>
<th>FeS$_2$ (marcasite)</th>
<th>FeS (mackinawite)</th>
<th>FeS (NiAs-troilite)</th>
<th>FeS (troilite)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bader charge (e$^-$)</td>
<td>ICOHP</td>
<td>Bond valence</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.67</td>
<td>-13.39</td>
<td>4.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.68</td>
<td>-13.85</td>
<td>4.27</td>
<td></td>
<td></td>
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<tr>
<td>-0.55</td>
<td>-10.56</td>
<td>3.78</td>
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</tr>
<tr>
<td>-0.98</td>
<td>-7.52</td>
<td>2.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.94</td>
<td>-6.85</td>
<td>2.05</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.commatsci.2019.04.001.

References


Fig. 7. the correlation between (a) integrated COHP (ICOHP), (b) Bader charge and bond valence of centered Fe atoms.

CRediT authorship contribution statement

Jinjia Liu: Writing - original draft. Aiju Xu: Writing - original draft, Funding acquisition. Yu Meng: Data curation. Yurong He: Writing - review & editing. Wen-Ping Guo: Conceptualization. Qing Peng: Writing - review & editing. Yong Yang: Supervision. Haijun Jiao: Writing - review & editing. Yongwang Li: Project administration, Supervision. Xiang-Dong Wen: Project administration, Funding acquisition, Writing - review & editing.

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