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# Achieving accurate energetics beyond (semi-)local density functional theory: Illustrated with transition metal disulfides, Cu\_{2}ZnSnS\_{4}, and Na\_{3}PS\_{4} related semiconductors

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# Achieving Accurate Energetics beyond (Semi-)Local Density Functional Theory: Illustrated with Transition Metal Disulfides, Cu<sub>2</sub>ZnSnS<sub>4</sub> and Na<sub>3</sub>PS<sub>4</sub> Related Semiconductors

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### ABSTRACT

Understanding, designing, and processing functional metal sulfides are significant challenges in part because of the high temperatures and pressures and the number of secondary phases encountered in these complex systems. In particular, the underlying thermochemical properties are not well understood that would allow prediction of equilibrium conditions and driving forces. In addition, accurate values for the energetics of metal sulfide systems is far from complete, suggesting application of density functional theory (DFT) calculations. Here, the results of an examination of 69 phases by DFT using 12 exchange-correlation (X-C) functionals indicate that (i) the key source of error in predicting the Gibbs energy of a phase is the enthalpy calculated at 0 K rather than entropy at finite temperatures from phonon calculations; and (ii) an improved prediction of the thermodynamic properties at 0 K relies on the selected non-local X-C functional such as the hybrid potential. Regarding metal sulfides, the present DFT results conclude that (1) the secondary phase Cu<sub>2</sub>ZnSn<sub>3</sub>S<sub>8</sub>, associated with the desired photovoltaic material Cu<sub>2</sub>ZnSnS<sub>4</sub>, is not stable at 0 K, but it becomes slightly stable with increasing temperature (i.e., > 800 K), primarily due to the vibrational entropy, which makes it difficult to be detected in a typical thin film growth process; (2) the hybrid X-C functional improves the predicted energetics for most of the layered transition metal disulfides such as TiS<sub>2</sub>, MoS<sub>2</sub>, and WS<sub>2</sub>, but not for the non-layered RuS<sub>2</sub>, OsS<sub>2</sub>, and IrS<sub>2</sub> as well as the layered PdS<sub>2</sub>; and (3) the formation of the solid-state electrolyte Na<sub>3</sub>PS<sub>4</sub> is thermodynamically favored. We further conclude that accurate energetics as a function of temperature for the materials of interest is feasible to be achieved beyond the semi-local DFT calculations with the key being enthalpy predicted at 0 K.

#### I. INTRODUCTION

Nanostructured metal sulfides have attracted considerable interest owing to their electrical and optical properties for various optoelectronic applications, including solar cells, photodetectors, transistors, light-emitting diodes, catalysts for water electrolysis, fuel cells, and lithium and sodium-ion batteries. Examples as well as the present focus of the intriguing metal sulfides include: (i) two dimensional (2D) transition metal disulfides with tunable electronic structure such as TiS<sub>2</sub>, ZrS<sub>2</sub>, VS<sub>2</sub>, NbS<sub>2</sub>, TaS<sub>2</sub>, MoS<sub>2</sub>, WS<sub>2</sub>, ReS<sub>2</sub>, RhS<sub>2</sub>, IrS<sub>2</sub>, PdS<sub>2</sub>, and PtS<sub>2</sub> [1]; (ii) solar cell thin films synthesized with earth abundant elements such as Cu<sub>2</sub>ZnSnS<sub>4</sub> and SnS [2,3]; and (iii) nonflammable solid-state electrolytes such as Na<sub>3</sub>PS<sub>4</sub> and Na<sub>11</sub>Sn<sub>2</sub>PS<sub>12</sub> rendering battery safer [4,5].

A key challenge in demonstrating these metal sulfide applications is the developing routes to synthesize these materials. Examples include large-area monolayers or heterostructures of 2D thin films with controlled layers and spatial homogeneity (e.g., MoS<sub>2</sub> and WSe<sub>2</sub>-MoS<sub>2</sub>) [6–8], phase-pure materials to achieve maximum device efficiency (e.g., pure Cu<sub>2</sub>ZnSnS<sub>4</sub> for high solar energy conversion efficiency [2] and ionic conductors Na<sub>10.8</sub>Sn<sub>1.9</sub>PS<sub>11.8</sub> with high transference number [5]). Understanding, designing, and processing functional metal sulfides, however, remain significant challenges in part because of the high temperature and pressures and the number of secondary phases encountered in these complex metal sulfide systems. For instance, there is a long standing debate about the phase stability of the secondary phase Cu<sub>2</sub>ZnSn<sub>3</sub>S<sub>8</sub> (associated with the desired photovoltaic material Cu<sub>2</sub>ZnSnS<sub>4</sub>), which has been proposed [9], but has not been confirmed experimentally in thin film growth using a typical growth process [10,11]. Another example is that it was thought that the superionic conductor

 $Na_{10}SnP_2S_{12}$  may be stable [12] in analogy to the Li-ion conductor  $Li_{10}GeP_2S_{12}$  [13]. However, recent work indicated that the proposed  $Na_{10}SnP_2S_{12}$  is unstable and it will decompose into  $Na_3PS_4$  and  $Na_{11}Sn_2PS_{12}$  based on experiments and density functional theory (DFT) calculations [5].

The rapidly emerging field of nanostructured metal sulfides would benefit from a rapid estimation of thermodynamic properties predicted possible from DFT based first-principles calculations. Figure 1 and Figure 2 compare enthalpies of formation ( $\Delta H$ ) for 81 binary sulfides predicted from DFT calculations to those from experimental measurements. Detailed data are shown in the Supplementary Excel file and Supplementary Fig. S1 [14]. Here, the error of enthalpy of formation ( $\Delta H_{error}$ ) is defined by,

$$\Delta H_{\rm error} = (\Delta H_{\rm MP} - \Delta H_{\rm SSUB}) / |\Delta H_{\rm SSUB}| \tag{1}$$

where  $\Delta H_{MP}$  is the enthalpy of formation from DFT calculations at 0 K using the semi-local exchange-correlation (X-C) functional of the generalized gradient approximation (GGA) [15], from the compilation of Materials Project (MP) database [16], and the value  $\Delta H_{SSUB}$  the enthalpy of formation at 298 K from the compilation of SGTE substance database (SSUB) [17], which is based on assessment of experimental data. Note that the small  $\Delta H$  difference between 0 K and 298 K (usually < 0.2 kJ kJ mol<sup>-1</sup> with mol indicating mole of atoms in the present work, see Sec. 3.2.2 for details) is ignored herein. Figure 1 and Figure 2 show that  $\Delta H_{MP}$  values are in general higher than  $\Delta H_{SSUB}$  values with  $\Delta H_{error}$  around 20% and up to 60%, e.g.,  $\Delta H_{error} = 41.8$  for Cu-containing sulfides. These figures indicate that thermodynamic properties of sulfides from the conventional DFT calculations using GGA are less accurate, similar conclusions were also drawn for other materials such as the Cu-Au alloys [18], the insulating and semiconducting solids [19], and the formation energies between calculations from the open quantum materials database (OQMD) and the SSUB database [20]. Despite awareness of the less accurate energetics from the conventional DFT calculations, little effort has been made to achieve accurate energetics in the DFT community compared with considerable efforts regarding electronic structure and energy band gap [21]. However, limited successes have been achieved concerning the prediction of enthalpy of formation in the Cu-Au system [18] and the Ba-Bi system [22] using nonlocal DFT. Inspired by these successes, by the long standing debates regarding phase stability in such as Cu<sub>2</sub>ZnSn<sub>3</sub>S<sub>8</sub> [10,11], and especially by the increased requirements of accurate Gibbs energy for high throughput thermodynamic modeling [23] using the CALPHAD (Computer Coupling of Phase Diagrams and Thermochemistry) approach with input from DFT calculations [24], the present work aims at exploring the feasibility to achieve accurate energetics by DFT and its beyond as illustrated with metal sulfides.

Less accurate DFT energetics are believed due to deficiencies in the selected X-C functional, which can be explained using the Jacob's ladder illustrated in Figure 3 [25,26]. It is expected that more and more accurate X-C potentials (functionals) can be developed from the rung of the local density approximation (LDA) as a function of electronic density (n), to the semi-local GGA (including both n and its gradient  $\nabla n$ ) and the meta-GGA (including n,  $\nabla n$ , and  $\nabla^2 n$ ), and ultimately to the rung of non-local hybrid potentials (exact Hartree-Fock exchange energy together with local or semi-local correlation) such as HSE03 [27] and HSE06 [28]. In practice, however, the accuracy of DFT calculations does not always increase from a lower to a higher rung as illustrated in Figure 3, because each row contains systematic errors between DFT and nature's true outcomes [29], requiring new strategies for functional development [30]. In addition to improving the description of exchange energy, the DFT + X methods can be used to better treat the non-local electron correlation [29]. For example, the DFT + D method accounts for dispersion interactions, i.e., the van der Waals interactions driven by electrons that are not symmetrically distributed in an atom or molecule. The DFT + U method accounts for strongly correlated electron system by introducing a Hartree-Fock like interaction as an on-site replacement of the X-C potentials such as LDA or GGA. Since the exact X-C functional is unknown, it necessary to test various proposed potentials for the material system of interest [31].

In the present work, achieving accurate energetics in metal sulfides has been explored as a function of temperature in terms of the local and semi-local density functional theory and beyond, i.e., using the conventional LDA and GGA and especially the hybrid X-C functionals and the DFT + X methods. Specifically the following questions have been addressed based on the current state of DFT applied to three categories of sulfides with a total of **69** phases (transition metal disulfides, as well as the photovoltaic material  $Cu_2ZnSnS_4$ , and the superionic conductor Na<sub>3</sub>PS<sub>4</sub> and their associated phases; see a complete list in the Supplementary Excel file [14]):

- What is the preferred X-C functional to achieve accurate energetics for metal sulfides?
- What is the more important for predicting the Gibbs energy based on the quasiharmonic approach [32]: the enthalpy at 0 K from DFT directly or the entropy at finite temperatures from phonon calculations?
- Which sulfides cannot be predicted sufficiently accurate relative to the presently calculated energetics?
- What is the best estimation of the Gibbs energy of Na<sub>3</sub>PS<sub>4</sub> using current DFT calculations? And *in particular*,

• Why is the expected Cu<sub>2</sub>ZnSn<sub>3</sub>S<sub>8</sub> absent in typical thin film growth processes?

#### **II. METHODOLOGY**

#### A. First-principles and phonon calculations

All DFT-based first-principles calculations in the present work were performed by the Vienna *Ab initio* Simulation Package (VASP) [33] with the ion-electron interaction described by the projector augmented wave (PAW) method [34]. Table 1 summarizes the twelve X-C functionals used in the present work, including the local X-C functional of LDA [35], the semi-local X-C functional of GGA developed by Perdew, Burke, and Ernzerhof (PBE) [15] and improved for densely packed solids and their surfaces (PBEsol or PS) [36], the hybrid functional of HSE06 with 25% non-local Hartree-Fock exchange and 75% semi-local exchange of GGA [28], the semi-empirical van der Waals correction as implemented by Grimme et al. (the D3 method) [37], and the DFT + U method as implemented by Dudarev et al. [38] to account for the strong on-site Coulomb interaction in transition metals (applied to Cu only in the present work). The effective U values for Cu were selected as 4 eV (labelled by U4) based on a previous DFT study of Cu<sub>2</sub>ZnSnS<sub>4</sub> [40].

In the VASP calculations, a plane wave cutoff energy of 360 eV was employed. The reciprocalspace energy integration was performed using the Gauss smearing method for structural relaxations and phonon calculations. Final calculations of total energies were performed by the tetrahedron method incorporating a Blöchl correction [41]. The self-consistency of total energy was converged to at least  $10^{-6}$  eV atom<sup>-1</sup>. In addition, the *k*-point mesh for each structure is given in the Supplementary Excel file [14]. The selected electronic configuration for each element was the same as the one used in Materials Project [16].

First-principles phonon calculations were performed for the selected polar materials of  $MoS_2$ ,  $WS_2$ ,  $SnS_2$ , ZnS,  $Cu_2SnS_3$ ,  $Cu_2ZnSnS_4$ ,  $Cu_2ZnSn_3S_8$ , NaS,  $P_4S_3$ ,  $P_4S_5$ , and  $Na_3PS_4$  using the supercell approach [42] as implemented in the YPHON code [43]. Here, the VASP code was again the computational engine in calculating force constants using the density functional perturbation theory or the finite differences method. The employed supercell for each structure and the corresponding *k*-point mesh and X-C functional are given in Supplementary Table S1 [14]. Since thermodynamic properties are the present focus, the longitudinal optical-transverse optical (LO-TO) splitting was ignored during phonon calculations.

# B. First-principles thermodynamics via the quasiharmonic approach

First-principles thermodynamic properties can be predicted by the quasiharmonic approach, i.e., the Helmholtz energy F as a function of volume V and temperature T is determined by [32],

$$F(V,T) = E(V) + F_{vib}(V,T) + F_{el}(V,T)$$
(2)

Here, F(V,T) is employed due to the facility of V instead of pressure P in DFT calculations.  $F_{el}(V,T)$  is the thermal electronic contribution, ignored in the present work since all the materials of interest are semiconductors (see Supplementary Table S1 [14]).  $F_{vib}(V, T)$  is vibrational contribution determined by phonon densities of states (DOS's, about 6 volumes were calculated for each compound). E(V) is the static energy at 0 K without the zero-point vibrational energy, which was determined by fitting the DFT calculated energy-volume (*E-V*) data points using a four-parameter Birch-Murnaghan equation of state (EOS) [32],

$$E(V) = k_1 + k_2 V^{-2/3} + k_3 V^{-4/3} + k_4 V^{-2}$$
(3)

where  $k_1$ ,  $k_2$ ,  $k_3$ , and  $k_4$  are fitting parameters. Correspondingly the three-parameter pressurevolume (*P-V*) EOS is given by [44],

$$P(V) = -\frac{\partial E}{\partial V} = a_1 V^{-5/3} + a_2 V^{-7/3} + a_3 V^{-3}$$
(4)

where  $a_1$ ,  $a_2$ , and  $a_3$  are fitting parameters. Equilibrium properties estimated by *E-V* and *P-V* EOS's include volume  $V_0$ , bulk modulus  $B_0$ , and the pressure derivative of bulk modulus B', plus the equilibrium energy  $E_0$  (cannot be estimated by *P-V* EOS). Note that the same properties from *E-V* EOS and *P-V* EOS can be used to judge the quality of DFT calculations [44]: the smaller the difference between the fitted properties, the better the quality will be. Usually six to nine reliable data points were used to estimate the equilibrium properties for each EOS fitting in the present work. In addition, the quality of EOS fitting was grouped into four levels: very good (negligible differences between EOS fittings and DFT calculations such as energy error < 1 meV), good (with differences e.g. > 1 meV for a few data points), fine (quite large differences with the fitted results for reference only).

#### C. Structures of metal sulfides and associated phases

For most of the sulfides and associated phases studied herein (i.e., 63 of 69), their structures can be found in Materials Project (MP) database [16]. Their MP ID numbers together with their space groups and atoms in the supercells for DFT calculations are listed in the Supplementary Excel file [14]. For example,  $MoS_2$  has an MP ID of mp-2815, space group  $P6_3/mmc$  (No. 194), and 6 atoms in the supercell. However, information is not available in Materials Project for six phases, whose structures were generated as follows. (1) Structures of  $Mo_xW_{1-x}S_2$  were built using the 6-, 12-, and 18-atom supercells based on the space group  $P6_3/mmc$  (No. 194) [45], resulting in 63 independent configurations according to the examination using ATAT software [46].

(2) The space group of  $Cu_4Sn_7S_{16}$  is  $R\overline{3}m$  (No. 166) with one of the Cu atoms partially occupied in Wyckoff site 6c (site occupancy factor, SOF = 0.5) [47]. Three Cu vacancies in site 6c were considered in an 81-atom supercell, resulting in four independent configurations shown by ATAT [46].

(3) Cu<sub>4</sub>SnS<sub>6</sub> also possesses the space group  $R\overline{3}m$  with partially occupied Sn in Wyckoff site 3a (SOF = 0.661) and Cu in site 6c (SOF = 0.326) [48]. Introduction of Sn- and Cu-vacancies in a 22-atom supercell results in nine independent configurations examined by ATAT [46].

(4) Cu<sub>4</sub>Sn<sub>15</sub>S<sub>32</sub> has the space group  $F\bar{4}3m$  (No. 216) with partially occupied Sn site (16e, SOF = 0.9375) [49], and hence one Sn vacancy was introduced in the structure.

(5) Cu<sub>2</sub>ZnSnS<sub>4</sub> has a kesterite structure with space group  $I\overline{4}$  (No. 82) as its ground state [50], and this structure was adopted herein.

(6) Structures of  $Cu_2ZnSn_3S_8$  were built based on two known structures. The first one is  $Cu_2CdSn_3S_8$  (or  $Cu_2FeSn_3S_8$ ) with space group  $I4_1/a$  (No. 88) [51,52], with details in Supplementary Table S2 [14]. Mixture of Zn and Sn in Wyckoff site 8d in terms of a 56-atom

supercell leads to 72 independent configurations based on ATAT [46]. The second structure is CuNi<sub>3</sub>Sn<sub>2</sub>S<sub>8</sub> with space group  $Fd\overline{3}m$  (No. 227) [53]. Assuming Cu in Wyckoff site 8a, S in 32f, and Sn/Zn in 16d results in 22 independent structures by ATAT [46]. Figure 4 shows the predicted energies of Cu<sub>2</sub>ZnSn<sub>3</sub>S<sub>8</sub> at 0 K in terms of the X-C functional of PS, indicating that the lowest energy configuration of Cu<sub>2</sub>ZnSn<sub>3</sub>S<sub>8</sub> originates from the space group  $I4_1/a$ , but belongs to a new space group  $R\overline{3}m$  (No. 166) with its crystallographic information given in Supplementary Table S2 [14]. This newly found structure will be adopted herein to predict properties of Cu<sub>2</sub>ZnSn<sub>3</sub>S<sub>8</sub>.

#### **III. RESULTS AND DISCUSSION**

#### A. Results of transition metal disulfides at 0 K

Table 2 summaries the enthalpy of formation ( $\Delta H$ ) for transition metal disulfides predicted by DFT at 0 K in comparison with experimental data at 298 K. In addition, Figure 5 shows the comparisons of volumes and  $\Delta H$  for these sulfides between calculations and experiments. Here the definitions of volume-error and  $\Delta H_{error}$  between calculations and experiments are similar to Eq. (1). Detailed DFT values in terms of PBE [16], PBE+D3, and PBE+D3+HSE06 are shown in the Supplementary Excel file [14], and the selections of these X-C functionals are based on our previous study of MoS<sub>2</sub> [45]. Experimental data are taken from the ICSD database [16] for volume and the SSUB database [17] for  $\Delta H$ .

Figure 5a shows that the van der Waals correction using the D3 method (with and without HSE06) improves significantly the predicted volumes for layered transition metal disulfides from  $TiS_2$  to  $ReS_2$  plus PdS<sub>2</sub> and PtS<sub>2</sub> [1], where the absolute values of volume-error decrease from

larger than 10% to lower than 2%. As expected, no significant improvements are observed for non-layered RuS<sub>2</sub> and OsS<sub>2</sub> and the partially layered RhS<sub>2</sub> and IrS<sub>2</sub> [1], i.e., the volume-errors change only about 2% with van der Waals correction (especially for the cases without HSE06). Note that the including of both HSE06 and D3 improves obviously the predicted volumes for RhS<sub>2</sub> and in particular for RuS<sub>2</sub> with its volume-error in the order of 0.1%. Figure 5b shows that the D3 method (without HSE06) cannot decrease the difference between the predicted values of  $\Delta H$  compared with experimental value. However, the hybrid X-C functional (PBE + D3 + HSE06) makes the predicted  $\Delta H$  better, i.e., the improvement is obviously for the layered sulfides from TiS<sub>2</sub> to ReS<sub>2</sub> plus PtS<sub>2</sub>, with  $\Delta H_{error}$  dropped more than 2% and especially for TiS<sub>2</sub> and ReS<sub>2</sub>. However, an exception is observed for the layered PdS<sub>2</sub> with  $\Delta H_{error} = -30\%$  by using HSE06, likely due to the  $\Delta H$  value predicted well by PBE ( $\Delta H_{error} = 0.4\%$ ). For non-layered or partially-layered disulfides (RuS<sub>2</sub>, OsS<sub>2</sub>, and IrS<sub>2</sub>, noting the absence of experimental data for RhS<sub>2</sub>) as well as a few exceptions of layered disulfides (here, PdS<sub>2</sub>), the results show that HSE06 underestimates their  $\Delta H$  values, increasing the discrepancy with experiments.

In general, results from Table 2, Figure 5, and the Supplementary Excel file [14] indicate that (i) the van der Waals correction needs to be considered for layered transition metal disulfides for a better prediction of structural properties such as equilibrium volume; and (ii) the hybrid X-C functional (e.g., HSE06) is necessary for a better description of thermodynamic properties (e.g., enthalpy of formation with the exception PdS<sub>2</sub> here). However, HSE06 underestimates  $\Delta H$  values for non-layered and partially-layered transition metal disulfides although their structural properties can be predicted better using HSE06.

Furthermore, Figure 6 shows the predicted enthalpy of mixing ( $\Delta H_{mix}$ ) of Mo<sub>x</sub>W<sub>1-x</sub>S<sub>2</sub> using PBE+D3 (all the predicted data are given in the Supplementary Excel file [14]). A test of the procedure with Mo<sub>0.5</sub>W<sub>0.5</sub>S<sub>2</sub> indicates that the hybrid HSE06 changes slightly the value of its  $\Delta H_{mix}$  value (< 0.002 kJ mol<sup>-1</sup>), and hence the time-consuming HSE06 may not be necessary. The negative  $\Delta H_{mix}$  values of Mo<sub>x</sub>W<sub>1-x</sub>S<sub>2</sub> suggest that it is possible to synthesize MoS<sub>2</sub>-WS<sub>2</sub> heterostructures. A complete thermodynamic guide to grow MoS<sub>2</sub>-WS<sub>2</sub> heterostructures requires  $\Delta H_{mix}$  of Mo<sub>x</sub>W<sub>1-x</sub>S<sub>2</sub> as a function of the number of monolayers and the temperature, which is beyond the scope of the present work.

## B. Results of Cu<sub>2</sub>ZnSnS<sub>4</sub> and associated phases at 0 K

Direct experimental measurements of the thermochemical properties are not available for  $Cu_2ZnSnS_4$  and  $Cu_2ZnSn_3S_8$ . Examination of various X-C functionals is hence performed for other sulfides related to  $Cu_2ZnSnS_4$  and  $Cu_2ZnSn_3S_8$ . Figure 7 shows the DFT predicted  $\Delta H$  values at 0 K for Cu-S compounds in comparison with data at 298 K from the SSUB database [17]. The results show that the semi-local PBE and PS give a less-accurate prediction of  $\Delta H$ , especially for  $Cu_2S$ . The difference between the calculated and measured  $\Delta H$ , i.e.,  $\Delta H_{diff}$ , is larger than 11 kJ mol<sup>-1</sup> for  $Cu_2S$  and 8 kJ mol<sup>-1</sup> for CuS. In terms of the hybrid X-C functional (PS + D3 + HSE06), calculated  $\Delta H$  values agree well with experiments with  $\Delta H_{diff}$  lower than 0.5 kJ mol<sup>-1</sup> for both  $Cu_2S$  and CuS. By considering the correction of DFT + U (PS + U4 and PS + U6), the predicted  $\Delta H$  values are also improved significantly, for example,  $\Delta H_{diff}$  is lower than 1 kJ mol<sup>-1</sup> for CuS. However, DFT calculations overcorrect the  $\Delta H$  values with all contributions included (i.e., PS + D3 + HSE06 + U6) due mainly to more systematic errors introduced between DFT and nature's true outcomes as aforementioned [29]. For example, the predicted  $\Delta H$  values

are more negative than the data from the SSUB database by 12.2 kJ mol<sup>-1</sup> for  $Cu_2S$  and by 3.8 kJ mol<sup>-1</sup> for CuS, respectively.

Figure 8 shows more comparisons between the calculated (at 0 K) and experimental (at 298 K)  $\Delta H$  values represented by  $\Delta H_{error}$ , defined by Eq. (1). Experimental data are taken from the reliable SSUB database [17] for Cu<sub>2</sub>S, CuS, Sn<sub>2</sub>S<sub>3</sub>, Sn<sub>2</sub>S, SnS, and ZnS and the measurements by using the electromotive forces method (emf) for Cu<sub>2</sub>SnS<sub>3</sub> and Cu<sub>4</sub>SnS<sub>4</sub> [54]. We believe that these two  $\Delta H$  values from emf measurements are less accurate as confirmed by CALPHAD modeling of the Cu-Sn-S system [55]. It is noted that the open circuit potential measurements of galvanic cells (emf data) directly measure Gibbs energy change. The enthalpy change is measured from the temperature derivative. The measured emf data and CALPHAD modelled  $\Delta H$  values are -40.4 and -44.4 kJ mol<sup>-1</sup> for Cu<sub>2</sub>SnS<sub>3</sub> and -36.4 and -39.0 kJ mol<sup>-1</sup> for Cu<sub>4</sub>SnS<sub>4</sub>, respectively. Figure 8 shows that PS + D3 + HSE06 predicts the best  $\Delta H$  values for Cu<sub>2</sub>SnS<sub>3</sub> and Cu<sub>4</sub>SnS<sub>4</sub> in comparison with the values by CALPHAD modeling (the dashed line showing  $\Delta H_{\text{error}} = 0$  should drop about 10% and 7% for Cu<sub>2</sub>SnS<sub>3</sub> and Cu<sub>4</sub>SnS<sub>4</sub>, respectively; see the short and dotted lines in Figure 8). Again, PBE and PS overestimate the  $\Delta H$  values with  $\Delta H_{error}$ larger than 20%. However, the contributions with both U6 and HSE06 (PS + D3 + HSE06 + U6) overcorrect the  $\Delta H$  values ( $\Delta H_{error}$  up to 40%). The DFT + U (PS + U4 or PS + U6) calculation also gives a good prediction of the  $\Delta H$  values (absolute value of  $\Delta H_{error} < 5\%$ ), suggesting a less expensive way to achieve accurate energetics by DFT calculations. It is also noted that LDA gives a reasonably good prediction with  $\Delta H_{error} < 10\%$ .

Table 3 summaries the Cu<sub>2</sub>ZnSnS<sub>4</sub> and Na<sub>3</sub>PS<sub>4</sub>-related reactions (labelled by R) examined in the present work. For example, R1 and R2 show the formation of Cu<sub>2</sub>ZnSn<sub>3</sub>S<sub>8</sub>; and R3 and R4 show the formation of Cu<sub>2</sub>ZnSnS<sub>4</sub>. Table 4 shows the predicted enthalpies of reaction ( $\Delta H_{reac}$ ) at 0 K (without zero point vibrational energy) with various X-C functionals for the reactions shown in Table 3. For Cu<sub>2</sub>ZnSn<sub>3</sub>S<sub>8</sub> via reaction R1, the predicted  $\Delta H_{reac}$  values are around but most of them are larger than zero, i.e., -0.10 ~ 1.49 kJ mol<sup>-1</sup> for the most reliable X-C functionals (Nos. 7-9 as well as 10-11 in Table 4), suggesting Cu<sub>2</sub>ZnSn<sub>3</sub>S<sub>8</sub> is probably not stable at 0 K with respect to Cu<sub>2</sub>ZnSnS<sub>4</sub> and SnS<sub>2</sub> based on the present DFT calculations. Regarding Cu<sub>2</sub>ZnSnS<sub>4</sub> via R3, the predicted  $\Delta H_{reac}$  values are all negative, indicating Cu<sub>2</sub>ZnSnS<sub>4</sub> is stable with respect to Cu<sub>2</sub>SnS<sub>3</sub> and ZnS and the most possible  $\Delta H_{reac} = -2.03$  to -2.79 kJ mol<sup>-1</sup> based on the X-C Nos. 7-9 (*cf.* Table 4).

For the other ternary compounds in the present work,  $Cu_4Sn_{15}S_{32}$  via R5 (*cf.* Table 4) shows quite positive  $\Delta H_{reac}$  values (> 1.73 kJ mol<sup>-1</sup>), indicating it is not stable at 0 K.  $Cu_4Sn_7S_{16}$  via R6 shows the negative  $\Delta H_{reac}$  values (0.23 ~ -0.68 kJ mol<sup>-1</sup>) for most of the X-C functionals, indicating it is probably stable at 0 K.  $Cu_4SnS_4$  via R7 shows either positive or negative  $\Delta H_{reac}$ values (1.78 vs. -1.14 kJ mol<sup>-1</sup>, *cf.* Table 4). Based on the phase diagram,  $Cu_4SnS_4$  is a stable phase, indicating a negative  $\Delta H_{reac}$  is reasonable (such as predicted via the X-C functional of PS + D3 + HSE06 + U6). Again, R1 via this X-C functional (No. 9) corresponds to a not-stable  $Cu_2ZnSn_3S_8$  with  $\Delta H_{reac} = 0.42$  kJ mol<sup>-1</sup>. For  $Cu_4SnS_6$  via R8, DFT calculations were performed by PS only, with  $\Delta H_{reac} = -0.48$  kJ mol<sup>-1</sup>, which indicates  $Cu_4SnS_6$  is probably stable at 0 K with respect to CuS and SnS<sub>2</sub>.

#### C. Results of metal sulfides at finite temperatures

Supplementary Fig. S2 [14] shows the variations of enthalpy of formation ( $\Delta H$ ) for seven sulfides (MoS<sub>2</sub>, WS<sub>2</sub>, Cu<sub>2</sub>ZnSnS<sub>4</sub>, Cu<sub>2</sub>ZnSn<sub>3</sub>S<sub>8</sub>, Cu<sub>2</sub>SnS<sub>3</sub>, SnS<sub>2</sub>, and ZnS) as a function of temperature from vibrational contribution only. The reference states are the standard element reference (SER) states, i.e., the enthalpy of pure element in its stable state at 298.15 K and 1 bar; and as examples, phonon densities of states (DOS's) at the equilibrium volumes of these sulfides are shown in Supplementary Fig. S3 [14]. Supplementary Fig. S2 shows that vibrational contribution to  $\Delta H$  decreases with increasing temperature, and it approaches to zero at room temperature (298 K) for these sulfides, i.e., the absolute  $\Delta H$  values < 0.2 kJ mol<sup>-1</sup>. Therefore, predicted  $\Delta H$  values at 0 K (without zero point vibration energy) are usually compared with experimental  $\Delta H$  at 298 K.

Analysis of stability for a phase of interest needs its energetics at finite temperatures. To verify predictions with experiments, Figure 9 shows the predicted entropies,  $\Delta H_T$ , and Gibbs energies of formation ( $\Delta G_T$ ) as a function of temperature for two Cu<sub>2</sub>ZnSnS<sub>4</sub>-related phases of SnS<sub>2</sub> and ZnS as well as two transition metal disulfides of MoS<sub>2</sub> and WS<sub>2</sub> in comparison with experiments (SSUB data) [17]. Note that (i) the  $\Delta H_{T=0K}$  values at 0 K are calculated by PBE + D3 + HSE06 and the vibrational contributions at finite temperatures are calculated by PBE+D3; (ii) the reference states for the calculated and experimental  $\Delta H_T$  and  $\Delta G_T$  are the aforementioned SER states , and (iii) the predicted data are also shown in the Supplementary Excel file [14]. Figure 9a shows that the predicted entropies agree well with values derived from experimental measurements, indicating that entropy can be predicted accurately in terms of the quasiharmonic phonon approach of Eq. (2), when anharmonic contribution is not a major issue at high temperatures [56]. The higher entropies of ZnS and SnS<sub>2</sub> with respect to those of WS<sub>2</sub> and MoS<sub>2</sub> can be understood from the higher phonon DOS's of ZnS and SnS<sub>2</sub> in the low frequency region (e.g., < 4 THz, see Supplementary Fig. S3 [14]), since vibrational entropy is proportional to phonon DOS as follows [44],

$$S \propto \int g(\omega) \ln(\omega) d\omega$$
 (5)

where  $\omega$  is the phonon frequency and  $g(\omega)$  the phonon DOS. Figure 9b and Figure 9c show that the variations of  $\Delta H_T$  and  $\Delta G_T$  have similar trends between calculations and experiments, where the differences between them stem mainly from the  $\Delta H_{reac}$  values at 0 K as aforementioned. This suggests that the major issue regarding the less accurate thermodynamic properties from the quasiharmonic phonon approach is caused by the predicted  $\Delta H$  at 0 K, at least for the present metal sulfides.

#### D. Phase stability of Cu<sub>2</sub>ZnSnS<sub>4</sub> and Cu<sub>2</sub>ZnSn<sub>3</sub>S<sub>8</sub> at finite temperatures

Figure 10 shows the Gibbs energies of reaction from vibrational contribution only,  $\Delta G_{\text{reac-vib}}$ , to form Cu<sub>2</sub>ZnSnS<sub>4</sub> and Cu<sub>2</sub>ZnSn<sub>3</sub>S<sub>8</sub> (R1 and R3 in Table 3, respectively) in terms of PBE + D3. With increasing temperature, the  $\Delta G_{\text{reac-vib}}$  values increase to e.g. 0.55 kJ mol<sup>-1</sup> at 1000 K for Cu<sub>2</sub>ZnSnS<sub>4</sub> but decrease to e.g. -1.3 kJ mol<sup>-1</sup> at 1000 K for Cu<sub>2</sub>ZnSn<sub>3</sub>S<sub>8</sub>. The variations of  $\Delta G_{\text{reac-vib}}$  as a function of temperature for Cu<sub>2</sub>ZnSnS<sub>4</sub> and Cu<sub>2</sub>ZnSn<sub>3</sub>S<sub>8</sub> can be understood from their phonon DOS's and Eq. (5). The phonon DOS of Cu<sub>2</sub>ZnSn<sub>3</sub>S<sub>8</sub> in the low frequency region (e.g. < 2 THz) is relatively higher than those of Cu<sub>2</sub>ZnSnS<sub>4</sub> and SnS<sub>2</sub> (see Supplementary Fig. S3 [14] and the reaction R1), resulting in a decreased  $\Delta G_{\text{reac-vib}}$  with increasing temperature. However, phonon DOS of Cu<sub>2</sub>SnS<sub>3</sub> at the low frequency region (e.g. < 2 THz) is even higher than that of Cu<sub>2</sub>ZnSnS<sub>4</sub> (see Supplementary Fig. S3 [14] and the reaction R3), resulting in an increased  $\Delta G_{\text{reac-vib}}$  with increasing temperature.

The results shown in Figure 10 and Table 4 indicate that Cu<sub>2</sub>ZnSnS<sub>4</sub> is stable with respect to Cu<sub>2</sub>SnS<sub>3</sub> and ZnS (i.e., the reaction R3) at finite temperatures, since  $\Delta H_{reac} = -2.03 \sim -2.79$  kJ mol<sup>-1</sup> at 0 K (see the discussion above and Table 4) and the small positive  $\Delta G_{reac-vib}$  value (*cf.* Figure 10, e.g., 0.55 kJ mol<sup>-1</sup> at 1000 K), resulting in a negative Gibbs energy of reaction in the temperature range of interest. The present DFT results agree well with the observed Cu<sub>2</sub>ZnSnS<sub>4</sub> phase diagram [9]. Regarding Cu<sub>2</sub>ZnSn<sub>3</sub>S<sub>8</sub>, Figure 10 and Table 4 support the conclusion that the compound is probably not stable with respect to Cu<sub>2</sub>ZnSnS<sub>4</sub> and SnS<sub>2</sub> (i.e. the reaction R1) at low temperatures since  $\Delta H_{reac} = -0.10 \sim 1.49$  kJ mol<sup>-1</sup> at 0 K (see the discussion above and Table 4). However, Cu<sub>2</sub>ZnSn<sub>3</sub>S<sub>8</sub> is probably stable at high temperatures due to the negative  $\Delta G_{reac-vib}$  value (*cf.* Figure 10, e.g., -1.3 kJ mol<sup>-1</sup> at 1000 K) caused by vibrational entropy that produces a negative (but still close to zero) Gibbs energy of reaction at high temperature. The present conclusion about phase stability of Cu<sub>2</sub>ZnSn<sub>3</sub>S<sub>8</sub> agrees with the proposed phase diagram involving Cu<sub>2</sub>ZnSn<sub>3</sub>S<sub>8</sub> [9], but it cannot be confirmed in a typical thin film growth process [10,11].

It should be mentioned that the effect of configurational entropy on Gibbs energy due to cation disorder [51,52,57] was ignored in both  $Cu_2ZnSnS_4$  and  $Cu_2ZnSn_3S_8$ , its effect can be cancelled to some extent during the analysis of reaction R1.

#### E. Results of Na<sub>3</sub>PS<sub>4</sub> and associated phases at 0 K

Figure 11 shows the errors in volume and  $\Delta H$  relevant to Na<sub>3</sub>PS<sub>4</sub> between DFT calculations (at 0 K) and experiments (at 298 K) [16,17]. Detailed data are shown in the Supplementary Excel file [14] and Table 5, and the definitions of errors are similar to Eq. (1). Figure 11a shows that the absolute errors for volume are all less than 10% except for P<sub>2</sub>S<sub>5</sub>, P<sub>4</sub>S<sub>3</sub>, and P<sub>4</sub>S<sub>5</sub> predicted by PBE; indicating that PBE is a bad choice for phosphorus sulfides. Figure 11b depicts that the errors in  $\Delta H$  are large (> 35% and up to 60%) for phosphorus sulfides but small for sodium sulfides (< 20%). The hybrid X-C functional of HSE06 improves the  $\Delta H$  predictions especially for sodium sulfides (Na<sub>2</sub>S, NaS, and NaS<sub>2</sub>) but less for phosphorus sulfides. According to Table 5, the predicted  $\Delta H$  values of Na<sub>3</sub>PS<sub>4</sub> at 0 K should be -100.63 kJ mol<sup>-1</sup> (from PS + D3 + HSE06) or even more negative. The reaction to form Na<sub>3</sub>PS<sub>4</sub> from sodium sulfides and phosphorus sulfides and phosphorus sulfides should possess the  $\Delta H_{reac}$  values around -28 kJ mol<sup>-1</sup> at 0 K (see R9 and R10 in Table 4).

Figure 12 shows the vibrational contribution to thermodynamic properties of reaction R10 to form Na<sub>3</sub>PS<sub>4</sub>, and the data to plot this figure are given in the Supplementary Excel file [14]. With increasing temperature, reaction Gibbs energy due to vibration ( $\Delta G_{reac-vib}$ ) increases to 3.1 kJ mol<sup>-1</sup> at 800 K, while both the reaction enthalpy and entropy decrease (up to around 350 K) and then increase. By considering both the negative  $\Delta H_{reac}$  values at 0 K (around -28 kJ mol<sup>-1</sup>) and the relatively small vibrational contribution, the formation of Na<sub>3</sub>PS<sub>4</sub> via R10 (or R9) is highly possible at finite temperatures albeit vibrational contribution makes it less favorite.

#### **IV. SUMMARY AND CONCLUSIONS**

Accurate energetics in terms of DFT calculations has been explored for metal sulfides and associated phases with the focus on the intriguing transition metal disulfides (such as MoS<sub>2</sub> and WS<sub>2</sub>), earth-abundant solar cell materials (such as Cu<sub>2</sub>ZnSnS<sub>4</sub> and Cu<sub>2</sub>ZnSn<sub>3</sub>S<sub>8</sub>), and sodium-ion solid-state electrolytes (such as Na<sub>3</sub>PS<sub>4</sub>). Examination of 69 phases using 12 X-C functionals draws two general conclusions. First, the "standard" local and semi-local X-C functionals (i.e., LDA and GGA) usually predict a higher enthalpy of formation (roughly 20%), and the improved predictions by DFT calculations rely on the non-local X-C functionals such as the hybrid one (e.g., HSE06). However, multiple improvements for the "standard" X-C functional may overcorrect the resulted energetics due to the introduction of systematic errors. For example, the consideration of DFT + D, DFT + U, and the exact exchange. Second, the key source of error in predicting Gibbs energy using the quasiharmonic approach is the enthalpy calculated at 0 K and not the entropy predicted by phonon at finite temperatures. It is worth mentioning that the present conclusions to achieve accurate energetics are not only validated for metal sulfides but also applicable for the materials of interest, such as the improved predictions concerning enthalpy of formation in the Cu-Au system [18] and the Ba-Bi system [22] using hybrid X-C functional.

Relevant to the present metal sulfides, the key findings are as follows. (1) The structure of  $Cu_2ZnSn_3S_8$  (associated with the desired solar cell material  $Cu_2ZnSnS_4$ ) can be represented by space group  $R\overline{3}m$ .  $Cu_2ZnSn_3S_8$  is most likely not stable at 0 K according to the present DFT calculations, but it becomes slightly stable with increasing temperature due mainly to vibrational entropy. However, the slightly energetic favorite  $Cu_2ZnSn_3S_8$  makes it difficult to be formed in a

typical thin film growth process. (2) Accurate energetics for layered transition metal disulfides can be predicted using a combined approach of DFT + D (here, the D3 method) and the hybrid X-C functional (here, the HSE06 method). However, this approach cannot predict well the energetics for non-layered transition metal disulfides (e.g., RuS<sub>2</sub> and OsS<sub>2</sub>) as well as a few layered disulfides (such as PdS<sub>2</sub>). (3) Unlike Cu<sub>2</sub>ZnSn<sub>3</sub>S<sub>8</sub> with a small reaction Gibbs energy in the level of  $\pm 1$  kJ mol<sup>-1</sup> (with respect to Cu<sub>2</sub>ZnSnS<sub>4</sub> and SnS<sub>2</sub>), the formation of Na<sub>3</sub>PS<sub>4</sub> is clearly favorable with the reaction Gibbs energy around -27 ~ -24 kJ mol<sup>-1</sup> at 0 K and finite temperatures (with respect to NaS, P<sub>4</sub>S<sub>3</sub>, and P<sub>4</sub>S<sub>5</sub>).

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# **Tables and Table Captions:**

Table 1. Various X-C functionals used in the present work, including the local X-C functional of LDA, the semi-local GGA (both PBE and PS), and the non-local cases of hybrid HSE, DFT + D3, and DFT + U (with the effective U = 4 eV and 6 eV for Cu).

,	- (
No.	X-C
1	LDA
2	PBE
3	PS
4	PBE+D3
5	PS+D3
6	PBE+D3+HSE
7	PS+HSE
8	PS+D3+HSE
9	PS+D3+HSE+U6
10	PS+U4
11	PS+U6
12	PS+D3+U6

Table 2. Enthalpies of formation ( $\Delta$ H, kJ mol<sup>-1</sup>) of transition metal disulfides from experiments (Expt.) at 298 K and first-principles calculations at 0 K using different X-C functionals.

TiS <sub>2</sub>	$VS_2$	$\leftarrow$ Transition metal disulfide									
-123.6	-84.2	$\leftarrow \Delta H$ by PBE (Materials Project) [16]									
-121.2	-79.6	$\leftarrow \Delta H$	$\leftarrow \Delta H \text{ by PBE+D3}$								
-135.7	-93.5	$\leftarrow \Delta H$	$\leftarrow \Delta H \text{ by PBE+D3+HSE06}$								
-135.7		$\leftarrow \Delta H$	by Expt.	(SGTE-	-SSUB)	[17]					
$ZrS_2$	NbS <sub>2</sub>	MoS <sub>2</sub>	TcS <sub>2</sub>	RuS <sub>2</sub>	RhS <sub>2</sub>	PdS <sub>2</sub>					
-146.6	-97.7	-83.4	-60.2	-53.4	-35.8	-26.4					
-144.8	-98.0	-83.4	-57.9	-60.3	-42.5	-27.4					
-161.8	-108.8	-88.6	-66.5	-84.7	-50.7	-38.9					
-192.3		-92.1		-68.6		-26.1					
$HfS_2$	$TaS_2$	$WS_2$	ReS <sub>2</sub>	$OsS_2$	IrS <sub>2</sub>	$PtS_2$					
-152.8	-101.5	-79.3	-55.2	-35.3	-37.8	-34.3					
-151.8	-98.0	-74.9	-50.3	-41.6	-40.1	-32.4					
-168.6	-109.2	-80.4	-58.4	-58.7	-54.1	-38.5					
	-118.0	-86.7	-59.6	-49.2	-44.4	-36.8					

	=
No.	Reactions
R1	$Cu_2ZnSnS_4 + 2 SnS_2 \rightarrow Cu_2ZnSn_3S_8$
R2	$3 \operatorname{SnS}_2 + \operatorname{Cu}_2 S + \operatorname{ZnS} \rightarrow \operatorname{Cu}_2 \operatorname{ZnSn}_3 S_8$
R3	$Cu_2SnS_3 + ZnS \rightarrow Cu_2ZnSnS_4$
R4	$SnS_2 + Cu_2S + ZnS \rightarrow Cu_2ZnSnS_4$
R5	$2 \operatorname{Cu}_2 \operatorname{SnS}_3 + 13 \operatorname{SnS}_2 \rightarrow \operatorname{Cu}_4 \operatorname{Sn}_{15} \operatorname{S}_{32}$
R6	$2 \operatorname{Cu}_2 \operatorname{SnS}_3 + 5 \operatorname{SnS}_2 \rightarrow \operatorname{Cu}_4 \operatorname{Sn}_7 \operatorname{S}_{16}$
R7	$Cu_2SnS_3 + Cu_2S \rightarrow Cu_4SnS_4$
R8	$4 \operatorname{CuS} + \operatorname{SnS}_2 \rightarrow \operatorname{Cu}_4 \operatorname{SnS}_6$
R9	$3 \operatorname{Na}_2 S + P_2 S_5 \rightarrow 2 \operatorname{Na}_3 PS_4$
R10	$24 \text{ NaS} + P_4S_3 + P_4S_5 \rightarrow 8 \text{ Na}_3PS_4$

Table 3. Various reactions related to Cu<sub>2</sub>ZnSnS<sub>4</sub> and Na<sub>3</sub>PS<sub>4</sub> examined in the present work.

Table 4. Calculated reaction enthalpies at 0 K without zero point vibrational energy (ZPE). Note that detailed data are given in the Supplementary Excel file.

X-C f	functionals	Reactio	on enthal	pies (kJ 1	mol <sup>-1</sup> ) for	r reactio	ons show	n in Tabl	e 3		
No.	Name	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10
1	LDA	-0.19		-1.01		1.92	-0.44				
2	PBE	2.02		-0.86						$-20.02^{a}$	-21.12 <sup>a</sup>
3	PS	-0.01	-3.17	-0.93	-5.52	2.05	-0.25	1.78	-0.48	-22.25	-22.89
4	PBE+D3	0.43		-1.36		2.04	0.23			-24.45	-23.26
5	PS+D3	-0.94		-1.34		1.73	-0.68			-25.52	-24.42
7	PS+HSE	1.49		-2.79							
8	PS+D3+HSE	-0.10	-4.82	-2.03	-8.26			0.25		-28.07	-27.22
9	PS+D3+HSE+U6	0.42	-4.43	-2.30	-8.48			-1.14			
10	PS+U4	0.68		-1.36							
11	PS+U6	0.94		-1.53							
12	PS+D3+U6							0.63			

<sup>a</sup> Based on the data of Materials Project [16].

Table 5. Enthalpies of formation ( $\Delta$ H) related to Na<sub>3</sub>PS<sub>4</sub> from experiments (Expt.) at 298 K and first-principles calculations at 0 K using different X-C functionals.

		0					
Method	Na <sub>2</sub> S	NaS	NaS <sub>2</sub>	$P_2S_5$	$P_4S_3$	$P_4S_5$	Na <sub>3</sub> PS <sub>4</sub>
PBE (MP) [16]	-103.58	-80.42	-56.59	-15.98	-14.53	-15.99	-85.27
PBE	-103.75	-80.59	-56.70				-85.38
PS	-102.56	-80.38	-58.14	-15.62	-12.66	-15.71	-86.77
PBE+D3	-109.17	-87.76	-64.39	-16.06	-13.78	-16.36	-92.89
PS+D3	-106.41	-85.36	-63.32	-15.48	-12.84	-16.38	-92.15
PS+D3+HSE06	-115.14	-92.63	-68.44	-17.81	-13.81	-17.22	-100.63
Expt. [17]	-124.83	-100.63	-68.62	-26.60	-32.03	-33.88	

## **Figures and Figure Captions:**

Li	Be											В	С	Ν
13.2	12.8													
Na	Mg	$\leftarrow$ Sulf	$\leftarrow$ Sulfide Al Si P							Р				
18.2	20.5	$\leftarrow \Delta H$ -	error (%)	), see Eq.	(1)							21.1	20.0	47.2
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn	Ga	Ge	As
	12.4		2.6		36.8	36.8	7.4		25.3	41.8	23.1	37.9	19.8	48.0
Rb	Sr	Y	Zr	Nb	Мо	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb
16.3	13.5		23.8		9.4		22.2		-9.7	49.3	17.2	25.2	23.6	39.9
Cs	Ba		Hf	Та	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi
16.0	14.6			14.0	8.5	7.3	28.3	16.7	5.4		_	-5.0	-5.4	-17.9
Fr	Ra	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm
		11.4	16.3	13.0	13.6									
		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md
			10.1		15.3		21.2							

Figure 1. Percentage error of enthalpy of formation ( $\Delta$ H-error) between DFT predictions from the Materials Project database ( $\Delta$ H<sub>MP</sub> at 0 K) [16] and experimental data from the SSUB database ( $\Delta$ H<sub>SSUB</sub> at 298 K) [17]. The average  $\Delta$ H-error values of sulfides are shown for each element and marked by the red (high), yellow (middle), green (low) color scale. Detailed data are given in the Supplementary Excel file, and the average  $\Delta$ H<sub>SSUB</sub> values are also given in Supplementary Fig. S1.



Figure 2. Summary of data points shown in Figure 1 as well as the Supplementary Excel file, i.e., the density of  $\Delta$ H-error based on 81 sulfides between DFT predictions and experiments.

"Heaven"	exact X-C
hybrid	n, $ abla n$ + exact exchange
meta-GGA	$n, \nabla n, \nabla^2 n$
GGA	$n, \nabla n$
LDA	n

Figure 3. Jacob's ladder of density functional approach for the X-C functional (energy), where n is electronic density and its first and second derivatives represented by  $\nabla n$ , and  $\nabla^2 n$ , respectively [25,26].



Figure 4. Calculated energetics of Cu<sub>2</sub>ZnSn<sub>3</sub>S<sub>8</sub> at 0 K based on space groups  $Fd\overline{3}m$  and  $I4_1/a$  using the X-C functional of PS. The lowest energy configuration, possessing a space group  $R\overline{3}m$  (No. 166), is also shown with its structure details provided in Supplementary Table S2.



Figure 5. Errors of (a) volume and (b) enthalpy of formation ( $\Delta$ H-error) at 0 K for transition metal disulfides: Comparison between DFT calculations (PBE from Materials Project [16], and the present results by PBE+D3 and PBE+D3+HSE06) and experimental data (based on the SSUB database [17] and the ICSD database [16]). Note that (1) experimental  $\Delta$ H data are absent for VS<sub>2</sub>, NbS<sub>2</sub>, TcS<sub>2</sub>, and RhS<sub>2</sub>; and (2) detailed data in this figure are provided in the Supplementary Excel file.



Figure 6. Calculated enthalpy of mixing  $(\Delta H_{mix})$  for the MoS<sub>2</sub>–WS<sub>2</sub> system in terms of the independent structures of 6-atom (Mo,W)<sub>2</sub>S<sub>4</sub>, 12-atom (Mo,W)<sub>4</sub>S<sub>8</sub>, and 18-atom (Mo,W)<sub>6</sub>S<sub>12</sub>, see detailed data in the Supplementary Excel file.



Figure 7. Enthalpies of formation ( $\Delta$ H) of the Cu-S compounds from DFT calculations at 0 K and experiments at 298 K based on the SSUB database [17]. All data are given in the Supplementary Excel file.



Figure 8. Errors of enthalpies of formation ( $\Delta$ H-error) of sulfides between DFT calculations at 0 K and experiments at 298 K [17,54]. Note that (i) all data are given in the Supplementary Excel file and (ii) experimental data derived from temperature dependent emf data for Cu<sub>2</sub>SnS<sub>3</sub> and Cu<sub>4</sub>SnS<sub>4</sub> are less accurate [54] and hence the dashed experimental line showing  $\Delta H_{error} = 0$  should drop about 10% and 7% for Cu<sub>2</sub>SnS<sub>3</sub> and Cu<sub>4</sub>SnS<sub>4</sub>, respectively; see the short and dotted lines based on our CALPHAD modeling for the Cu-Sn-S system [55] and the discussion in the main text.



Figure 9. Calculated (a) entropies S, (b) enthalpies H, and (c) Gibbs energies G of SnS<sub>2</sub>, ZnS, MoS<sub>2</sub>, and WS<sub>2</sub> compared with experiments (SSUB database) [17]. Note that (i) enthalpies of formation at 0 K are calculated by PBE+D3+HSE06 and vibrational contributions are calculated by PBE+D3; (ii) the reference states for the calculated and experimental H and G are the standard element reference, i.e., the enthalpy of pure element in its stable state at 298.15 K and 1 bar. DFT results are given in the Supplementary Excel file.



Figure 10. Vibrational contribution to reaction Gibbs energies to form  $Cu_2ZnSnS_4$  and  $Cu_2ZnSn_3S_8$  (reactions 1 and 3 in Table 3, respectively). The employed X-C functional is PBE+D3 and data are also given in the Supplementary Excel file.



Figure 11. Errors of (a) volume and (b) enthalpy of formation ( $\Delta$ H-error) at 0 K related to Na<sub>3</sub>PS<sub>4</sub>: Comparison between DFT calculations (PBE from Materials Project [16] and the present results for others) and experimental data (based on the SSUB database [17] and the ICSD database [16]). Note that (1) experimental  $\Delta$ H data are absent for Na<sub>3</sub>PS<sub>4</sub>; and (2) detailed data in this figure are given in the Supplementary Excel file.



Figure 12. Vibrational contribution to reaction Gibbs energy  $\Delta G$ , enthalpy  $\Delta H$ , and entropy  $\Delta S$  to form Na<sub>3</sub>PS<sub>4</sub> in terms of the reaction 10 in Table 3. The employed X-C functional is PS+D3 and data are also given in the Supplementary Excel file [14].