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Reaction thermochemistry of metal sulfides with GGA and GGA+*U* calculations

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Sulfurization reaction energies of 24 metal sulfide (M-S) systems including M = Li, Na, K, Mg, Ca, Sr, Ba, Zn, Al, Ti, Mn, Fe, Co, Ni, Cu, Mo, Rh, Pd, Ir, Pt, La, Ce, Th, and U are evaluated using generalized gradient approximation (GGA) and GGA+U calculations. Our results indicate that unlike metal oxides and halides, GGA reaction energy predictions can be improved consistently only if separate energy corrections are used for S in sulfide anion (S^{2-}) and disulfide anion (S_2^{2-}) because of the existence of covalent $^{-}$S–S^{-} bonds in the latter anion. Enumerating all possible sulfurization reactions between pairs of d- and f-block metal sulfides within each M-S system, we predict effective U values for GGA+U thermochemistry and confidence intervals for these U values. We find that applying U on the d or f orbitals of these nonsimple metal ions consistently improves GGA reaction energy predictions for most of these systems, except for the reactions where the reaction energy is insensitive to U applied to the metal M, and only the S anions perform the redox activity (i.e., change the nominal oxidation state). We show that GGA+U calculations with the predicted U values and anion-dependent systematic energy corrections provide a significant improvement over standard, uncorrected GGA in predicting cell voltages of a variety of M-S based battery systems including Li/FeS_2, Li/TiS_2, Li/Mo_6S_8, and Mg/Mo_6S_8.

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I. INTRODUCTION

Metal sulfides (M-S) are of high technological interest for a wide range of applications in electronic and optical devices [1–6], catalysis [7–10], and energy harvesting and storage [11–14]. Because of their high-energy density and ease of accessibility compared to conventional electrode materials [11,15–17], metal sulfides have long been investigated as cathode materials for secondary batteries [12–14,18,19], but their low cell voltage [17,19–21] and short cycle life [15,18,22] hinder their widespread applications. First-principles thermodynamic information has already become a critical part of designing energy materials [19,23–31], and can play a significant role in overcoming such obstacles that M-S systems currently face in technological applications. Despite the ever-growing interest in M-S systems, the thermochemical accuracy of available first-principles approaches in these systems remains largely unexplored.

In density functional theory (DFT) calculations, the most commonly used exchange-correlation (XC) functionals are the local density approximation (LDA) and generalized gradient approximation (GGA) [32]. While these (semi)local XC functionals can successfully describe the electronic and thermodynamic properties of a wide spectrum of materials, they yield non-negligible errors when describing systems with strong electron correlations, molecular systems, and reactions involving transfer of electrons between dissimilar environments [33–37]. In DFT-based reaction thermochemistry of metal compounds, errors are mostly assumed to arise from two different sources: (i) systematic errors presumably associated with the DFT description of the anion or its molecular state that can be fixed by applying a constant energy correction, and (ii) electron self-interaction related problems in LDA or GGA that can be mitigated by applying a separate Hubbard U on the d or f manifolds [38–41]. This scheme of separating errors was first proposed by Wang *et al.* [39] for redox reactions of transition metal (TM) oxides using GGA+U. In the work of Wang *et al.*, a correction factor is found *a priori* for the O_2 molecule by fitting its chemical potential to experimental formation enthalpies of a set of simple metal oxides. This systematic correction of error associated with the gaseous molecules in reactions was later extended to halides, nitrides, and hydrides [40]. Elemental chemical potential correction schemes are today extended beyond gaseous molecules and widely used in high-throughput DFT frameworks to improve the accuracy of DFT reaction energies [42–44]. The self-interaction error associated with d- and f-metal ions in metal compounds in a redox reaction, on the other hand, can be at least partially mitigated using the DFT+U separately [39,45]. Aykol and Wolverton [41] further extended the approach by Wang *et al.* to take into account the local environment (i.e., the oxidation state of TM and the coordinating anion) dependence of U values which showed improvements in reaction thermochemistry over constant-U GGA+U calculations of 3d-metal oxides and fluorides.

The reference state for elemental sulfur is a molecular solid commonly recognized as α-sulfur, which is also known as the octasulfur ring structure [46], where sulfur atoms bond covalently to two nearest neighbors. However, unlike in metal oxide or fluoride compounds where O and F stay in their nominal oxidation states and bind mostly electrostatically with the metal ions, bonds in M-S, especially the nonsimple metal sulfides, often have more covalent character due to the lower electronegativity of S and their accessible d states [47]. Therefore, the oxidation state of S in a M-S compound can deviate from the nominal value of −2, and S can commonly form two different types of anions: namely, S^{2-} and S_2^{2-}. These different S anions naturally lead to bonds of different character in M-S compounds. Thus, when calculating the energy of a sulfurization reaction, the extent of error cancellation between the reference state α-S and these two different types of S anions need not be the same. Therefore, a correction factor for S will have distinct values for S^{2-} and S_2^{2-}.

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In this work, we perform a systematic analysis of the accuracy of GGA and GGA+U thermochemistry of redox reactions of 24 M-S systems with M = Li, Na, K, Mg, Ca, Sr, Ba, Zn, Al, Ti, Mn, Fe, Co, Ni, Cu, Mo, Rh, Pd, Ir, Pt, La, Ce, Th, and U by (i) finding anion-dependent correction factors (ACFs) for sulfide anions (S^{2-} and S_2^{2-}) in simple metal sulfides, (ii) then calculating all sulfurization reaction energies as a function of U in each d- and f-metal sulfide system (15 systems in total) using ACFs, and (iii) carrying out a systematic comparison of calculated energies with experiments to assess the accuracy of GGA+U in d- and f-block metal sulfide thermochemistry. We extract constant thermochemical U values (which depend solely on chemical identify of the metal ion) and their confidence intervals for these d- and f-block metal sulfide systems. Finally, we illustrate the utility of this approach by showing that our corrected DFT energetics significantly increase the accuracy for voltage predictions in a variety of M-S battery systems.

II. METHODOLOGY

A. DFT calculations

In all first-principles calculations, we used the Perdew-Burke-Enzerhof (PBE) [48] formulation of GGA and projected augmented wave (PAW) potentials as implemented in Vienna *ab initio* simulation package (VASP) [49–52]. We used the following pseudopotentials: Li_sv, Na_pv, K_sv, Mg, Ca_sv, Sr_sv, Ba_sv, Zn, Al, Ti_sv, Mn_pv, Fe, Co, Ni, Cu, Mo_sv, Rh_pv, Pd, Ir, Pt, La, Ce, Th, U, and S. A cutoff energy of 520 eV and an approximate k-point density of 8000 k-points per reciprocal atom were used. We have fully relaxed all degrees of freedom for all the compounds, and obtained the total energy with a final static run. For all calculations of d- and f-block metal sulfides, we used Dudarev's rotationally invariant DFT+U approach [53].

We employed the U-ramping scheme developed by Meredig *et al.* [54], especially for f-metal sulfides to avoid metastable electronic occupations. For all nonsimple metal sulfide compounds in this work, we applied U values from 0 to 8 eV with 1-eV intervals on d or f manifolds. At each U value, we initiated the calculations with different initial spin arrangements corresponding to different magnetic structures: ferromagnetic (FM), antiferromagnetic (AFM), nonmagnetic (NM), and ferrimagnetic (ferri). To enumerate all symmetrically unique antiferromagnetic and ferrimagnetic spin arrangements, we utilized the method by Hart *et al.* [55], and conducted about a total of 8000 DFT calculations on different magnetic structures of d- and f-block metal sulfides with different U values applied. We used the lowest-energy magnetic configuration at each U value for each compound as input to the calculation of reaction energies.

B. Anion-dependent systematic error correction

To calculate anion-dependent systematic corrections for sulfur, we used a similar approach as reported by Wang *et al.* [39] and Grindy *et al.* [40]. We separated the self-interaction related errors associated with d and f electrons of nonsimple metal ions from any systematic error associated with sulfur in its molecular solid S_8(α ring) form and S anions S_2^{2-} and S^{2-} by only considering formation reactions of binary simple metal sulfides with no or closed d and f shells. The formation reaction for a simple metal binary compound from a metal M and S can be written generically as

$$M + x\mathrm{S} \rightarrow M\mathrm{S}_x, \tag{1}$$

where the sulfide is denoted as $M\mathrm{S}_x$ using only one stoichiometric coefficient x for simplicity. By neglecting the relatively small PV contribution to enthalpy for solids, the DFT calculated formation enthalpy of $M\mathrm{S}_x$ can be expressed as

$$\Delta H^{\mathrm{DFT}}_{f,M\mathrm{S}_x} = E^{\mathrm{DFT}}_{M\mathrm{S}_x} - E^{\mathrm{DFT}}_{M} - xE^{\mathrm{DFT}}_{\mathrm{S}}, \tag{2}$$

where E^{DFT}_p represents the DFT total energy of phase p. Assuming that any deviation of DFT calculated formation enthalpies from experimental data for simple metal sulfides can be corrected with a systematic correction factor $\hat{C}_i$ per S where i denotes the particular form of S anion (S_2^{2-} or S^{2-}) present in the compound, we can write

$$\Delta H^{\mathrm{DFT}}_{f,M\mathrm{S}_x} = \Delta H^{\mathrm{expt}}_{f,M\mathrm{S}_x} + x\hat{C}_i, \tag{3}$$

where $H^{\mathrm{DFT}}_{f,M\mathrm{S}_x}$ represents the DFT calculated formation enthalpy of $M\mathrm{S}_x$ and $H^{\mathrm{expt}}_{f,M\mathrm{S}_x}$ denotes the experimental formation enthalpy. To fit $\hat{C}_i$ and its associated uncertainty $\sigma_{\hat{C}_i}$, we used a least-squares fitting algorithm [68] where

$$\hat{C}_i = \overline{\Delta H}^{\mathrm{DFT}}_{f} - \overline{\Delta H}^{\mathrm{expt}}_{f}, \tag{4}$$

$$\sigma^2_{\hat{C}_i} = 1\Big/\sum \omega(j). \tag{5}$$

Here, the coefficient $\omega(j)$ of compound j is calculated as $(\sigma_{\Delta H^{\mathrm{expt}}_{f,j}})^{-2}$, where $\sigma_{\Delta H^{\mathrm{expt}}_{f,j}}$ is the reported uncertainty in experimental formation enthalpy of compound j in our training set of simple metal compounds that have the anion i. $\overline{\Delta H}^{\mathrm{expt}}_{f}$ and $\overline{\Delta H}^{\mathrm{DFT}}_{f}$ are simply the weighted means of experimental and DFT formation enthalpies of compounds in the training set, calculated as $\sum[\omega(j) \times \Delta H^{\mathrm{expt}}_{f,j}]/\sum \omega(j)$ and $\sum[\omega(j) \times \Delta H^{\mathrm{DFT}}_{f,j}]/\sum \omega(j)$, respectively [68]. Using two groups of simple metal sulfides and corresponding $\Delta H^{\mathrm{expt}}_{f,M\mathrm{S}_x}$ listed in Table I, we fitted separate correction factors $\hat{C}_{S_2^{2-}}$ and $\hat{C}_{S^{2-}}$ for S_2^{2-} and S^{2-}, respectively. Assuming these correction factors are transferable from simple metal sulfides to d- and f-block metal sulfides, the total energy of a d- or f-block metal sulfide calculated by DFT+U can then be corrected by subtracting $\hat{C}_{S_2^{2-}}$ or $\hat{C}_{S^{2-}}$ for each S atom, depending on the type of S anions present in the compound. Different from the method of Wang *et al.*, where they applied the systematic error correction factor on DFT calculated energy of elemental sulfur, we applied the ACFs on calculated energies of metal sulfides, which allows separate corrections based on sulfur anion states.

C. Sulfurization reaction enthalpies with GGA+U

To mitigate the self-interaction error associated with d- and f-metal ions in GGA, and subsequently improve the accuracy of GGA reaction enthalpies, we applied an effective U parameter on the d or f electrons of the nonsimple metal

TABLE I. Experimental formation enthalpies and space groups of simple metal sulfides used for finding the anion-dependent systematic error correction factors (ACFs) for sulfur. The first nine compounds were employed while fitting for $\hat{C}_{S^{2-}}$ and the last three were employed while fitting for $\hat{C}_{S_2^{2-}}$.

Compound	Space group	ΔH_f^{expt} (kJ/mol)
Li_2S	$Fm\bar{3}m$ [56]	-453.8 ± 2.1[a,d]
Na_2S	$Fm\bar{3}m$ [57]	-350.2 ± 12.6[a,d]
K_2S	$Fm\bar{3}m$ [58]	-360.2 ± 12.6[a,d]
MgS	$Fm\bar{3}m$ [59]	-344.6 ± 4.2[b,e]
CaS	$Fm\bar{3}m$ [60]	-472.1 ± 2.9[b,e]
SrS	$Fm\bar{3}m$ [60]	-476.6 ± 17[b,e]
BaS	$Fm\bar{3}m$ [61]	-462.7 ± 2.1[b,e]
ZnS	$F\bar{4}3m$ [62]	-195.2 ± 2.5[a,d]
Al_2S_3	$P6_1$ [63]	-647.4 ± 3.8[b,d]
Li_2S_2	$P6_3/mmc$ [64][g]	-438.1[c,f,h]
Na_2S_2	$P6_3/mmc$ [64]	-397.0 ± 8[b,f]
K_2S_2	$P\bar{6}2m$ [64]	-432.2[c,f,h]

[a] Experimental data from Kubaschewski *et al.* [65].

[b] Experimental data from JANAF thermochemical tables [66].

[c] Experimental data from The NBS Table of Chemical Thermodynamic Properties [67].

[d] Extrapolated to 0 K from 298 K formation enthalpy using the experimental entropy and heat capacity as described in Ref. [41].

[e] 0 K formation enthalpy in the cited reference.

[f] 298 K formation enthalpy.

[g] This structure is derived from Na_2S_2 structure.

[h] Experimental uncertainty not reported; however, we imposed the same uncertainty level of Na_2S_2 experimental data for calculation.

element M in its different sulfides in the following sulfurzation reaction:

$$MS_a + (b-a)\mathrm{S} \rightarrow MS_b. \tag{6}$$

Then, we are able to calculate the enthalpy of Eq. (6) by neglecting the small PV contribution to enthalpies of solids as a function of U as

$$\Delta H_{\text{reaction}}^{\text{DFT}}(U) = \left[E_{MS_b}^{\text{DFT}}(U) - b \cdot \hat{C}_i\right] - \left[E_{MS_a}^{\text{DFT}}(U) - a \cdot \hat{C}_j\right] - (b-a)E_{\mathrm{S}}^{\text{DFT}}, \tag{7}$$

where a and b are the stoichiometric coefficients of the d- or f-block metal sulfides MS_a and MS_b, and $\hat{C}_i$ and $\hat{C}_j$ denote the corresponding ACF of sulfur in these compounds, respectively. Therefore, to apply the suitable ACF, we need to determine the type of sulfur anion in a given nonsimple metal sulfide. We differentiated S^{2-} and S_2^{2-} by investigating the possible existence of sulfur-sulfur bonding. In S_2^{2-}, sulfur bonds with another sulfur covalently, whereas in M-S with only S^{2-}, the metal directly binds with sulfur mostly electrostatically. According to Knop *et al.* [69], the observed range of S-S bond lengths is 2.03 to 2.36 Å. Therefore, we set the threshold value of the sulfur-sulfur distance to be below 2.4 Å to have existence of S_2^{2-}, otherwise, we would assume we only have S^{2-}. By examining the experimental structures described in Table II, and conducting a broad literature survey on each compound, the anion types of sulfur in all the d- and f-metal sulfides in this work are summarized in Table II. Validating our approach above on classifying the S anion, we found that for all 16 compounds for which we could find an experimental report specifying the type of the S anion in the compound (as cited in Table II), our classification agreed with the experimental report.

Using the experimental formation enthalpies of the two compounds in the sulfurization reaction in Eq. (6), we can also calculate the experimental enthalpy for the same reaction as

$$\Delta H_{\text{reaction}}^{\text{expt}} = \Delta H_{f,MS_b}^{\text{expt}} - \Delta H_{f,MS_a}^{\text{expt}}. \tag{8}$$

Comparing this experimental reaction enthalpy to that calculated as a function of U in Eq. (7), we can find an effective U value for M that yields the most accurate reaction enthalpy prediction. The experimental formation enthalpies and crystal structures of the d- and f-block metal sulfides involved in this work are summarized in Table II.

There are two sources of uncertainties involved in this "U-fitting" procedure described above. First, when calculating the experimental reaction enthalpy of Eq. (6) using Eq. (8), uncertainties in d- and f-block metal experimental formation enthalpies propagate, and the corresponding combined uncertainty for experimental reaction enthalpy can be calculated as

$$\sigma_{\Delta H^{\text{expt}}} = \sqrt{\left(\sigma_{MS_a}^{\text{expt}}\right)^2 + \left(\sigma_{MS_b}^{\text{expt}}\right)^2}, \tag{9}$$

where σ_i^{expt} denotes the reported uncertainty in experimental formation enthalpy of compound i. For compounds where the uncertainty of the experimental formation enthalpy is not reported, we imposed an average uncertainty obtained from all other compounds in Table II with a reported σ^{expt}. Second, we also have an uncertainty $\sigma_{\hat{C}_i}$ associated with the ACFs for S as described in Sec. II B.

The confidence interval for U now encloses a two-dimensional space defined by variables $\sigma_{\hat{C}}$ and $\sigma_{\Delta H^{\text{expt}}}$ as illustrated in Fig. 1, where the DFT calculated reaction enthalpy [Eq. (7)] versus U changes into a band with $\sigma_{\hat{C}}$. The $\sigma_{\Delta H^{\text{expt}}}$ value, on the other hand, describes the range for the experimental enthalpy. Eventually, since both uncertainties introduce only linear transformations, the confidence interval for the fitted U can be assessed by finding the extrema of fitted-U value considering different combinations of $\pm\sigma_{\hat{C}}$ and $\pm\sigma_{\Delta H^{\text{expt}}}$ shown schematically as *fitted maximum* and *minimum* in Fig. 1.

III. RESULTS AND DISCUSSION

A. Anion-dependent systematic correction factors (ACFs)

Using the approach described in Sec. II B, we determined the ACFs for sulfur anions as 0.365 ± 0.024 eV/S and 0.492 ± 0.009 eV/S for S_2^{2-} and S^{2-}, respectively, as shown in Fig. 2. The correction factor for S_2^{2-} is significantly different from that for S^{2-}. This difference originates from different bonding conditions involving S_2^{2-} and S^{2-} anions. In metal sulfides with only S^{2-}, sulfur atoms bond directly with metal ions, and remain fully coordinated with them. However, in compounds with S_2^{2-}, two sulfur atoms bind covalently to form an anion group of the form $^{-}\mathrm{S}-\mathrm{S}^{-}$, and the M-S bonds these S atoms can form now involve one electron unlike two in S^{2-}. Relative

TABLE II. Experimental formation enthalpies, space groups, and anion types of sulfur atoms of *d*- and *f*-block metal sulfides used in GGA+*U* calculations.

Compound	Space group	ΔH_f^{expt} (kJ/mol)	Anion type	Anion type references
TiS	$P6_3/mmc$ [70]	-262.9 ± 29.3[a,e], -238[b,f]	S^{2-}	
TiS_2	$P\bar{3}m1$ [71]	-394.4 ± 33.5[a,e]	S^{2-}	[72]
MnS	$Fm\bar{3}m$ [73]	-203.0 ± 2.1[a,e]	S^{2-}	
MnS_2	$Pa\bar{3}$ [74]	-209.1[c,e]	S_2^{2-}	
FeS	$P\bar{6}2c$ [75]	-102.2 ± 0.8[d,g]	S^{2-}	[76]
Fe_7S_8	$C2/c$ [77]	-743.4[c,g]	S^{2-}	
FeS_2	$P\bar{1}$ [78]	-167.9 ± 2.1[d,g]	S_2^{2-}	[76]
CoS	$P6_3/mmc$ [79]	-82.8[b,f]	S^{2-}	[76]
CoS_2	$Pa\bar{3}$ [80]	-141.3 ± 8.4[a,e]	S_2^{2-}	[76]
NiS	$R3m$ [79]	-87.1 ± 6.3[d,g]	S^{2-}	[76]
Ni_3S_4	$Fd\bar{3}m$ [81]	-274.4 ± 25.1[a,e]	S^{2-}	[82]
NiS_2	$Pa\bar{3}$ [83]	-118.1 ± 16.7[c,e]	S_2^{2-}	[76]
Cu_2S	$P4_32_12$ [84]	-62.5 ± 1.7[a,e]	S^{2-}	
CuS	$P6_3/mmc$ [85]	-42.4 ± 4.2[a,e]	$\frac{2}{3}S_2^{2-}$, $\frac{1}{3}S^{2-}$	[86]
Mo_2S_3	$P2_1/m$ [87]	-386.7 ± 8.4[a,e]	S^{2-}	
MoS_2	$P6_3/mmc$ [88]	-273.3 ± 2.5[d,g]	S^{2-}	[89]
Rh_3S_4	$C2/m$ [90]	-327.8[a,e]	$\frac{1}{3}S_2^{2-}$, $\frac{2}{3}S^{2-}$	[91]
Rh_2S_3	$Pbcn$ [92]	-241.6[a,e]	S^{2-}	[93]
PdS	$P4_2/m$ [94]	-61.7 ± 6.3[a,e]	S^{2-}	
PdS_2	$Pbca$ [95]	-64.2 ± 12.6[a,e]	S_2^{2-}	[96]
Ir_2S_3	$Pbcn$ [97]	-238.4[a,e]	S^{2-}	
IrS_2	$Pnam$ [98]	-121.0[a,e]	$\frac{1}{2}S_2^{2-}$, $\frac{1}{2}S^{2-}$	[99]
PtS	$P4_2/mmc$ [100]	-74.2 ± 2.5[a,e]	S^{2-}	
PtS_2	$P\bar{3}m1$[101]	-98.2 ± 2.5[a,e]	S^{2-}	
LaS	$Fm\bar{3}m$ [102]	-461.9 ± 5.0[a,e]	S^{2-}	[103]
La_2S_3	$Pnma$ [104]	-1039 ± 35[105][f]	S^{2-}	
CeS	$Fm\bar{3}m$ [102]	-444.8 ± 8.4[a,e]	S^{2-}	
Ce_3S_4	$I\bar{4}3d$ [106]	-1614.9 ± 20.9[a,e]	S^{2-}	
ThS	$Fm\bar{3}m$ [106]	-389.0 ± 6.3[a,e]	S^{2-}	
Th_2S_3	$Pbnm$ [106]	-1057.2 ± 12.6[a,e]	S^{2-}	
ThS_2	$Pbnm$ [106]	-613.1 ± 33.5[a,e]	S^{2-}	
US	$Fm\bar{3}m$ [106]	-306.5 ± 6.7[a,e]	S^{2-}	
US_2	$P\bar{6}2m$ [107]	-510.2 ± 6.3[a,e]	S^{2-}	
US_3	$P2_1/m$ [108]	-527.8 ± 33.5[a,e]	$\frac{2}{3}S_2^{2-}$, $\frac{1}{3}S^{2-}$	[108]

[a] Experimental data from Kubaschewski *et al.* [65].

[b] Experimental data from The NBS Table of Chemical Thermodynamic Properties [67].

[c] Experimental data from Goos *et al.* [109].

[d] Experimental data from JANAF thermochemical tables [66].

[e] Extrapolated to 0 K from 298 K formation enthalpy using the experimental entropy and heat capacity as described in Ref. [41].

[f] 298 K formation enthalpy.

[g] 0 K formation enthalpy in the cited reference.

to the molecular solid α-S reference state composed solely of S-S bonds, fewer S-S bonds need to be broken to form the S_2^{2-} anion compared to S^{2-}. As a result, some partial error cancellation is expected to be already present for the formation process of metal sulfides with S_2^{2-} from α-S, which can explain why S_2^{2-} has a smaller ACF than S^{2-}.

Aside from the simple chemical arguments above, ACFs in fact improve the accuracy of DFT formation enthalpies of simple metal sulfides significantly. The improvement is much clearer when we fit a constant correction for S using the method of Wang *et al.* [39] (in analogy with the chemical potential correction methods employed in Refs. [28,43,44]) and compare that to ACFs. Fitting to all the sulfides included in Table I, we obtained a Wang *et al.* type correction factor of 0.477 eV/S. This single, constant correction factor results in mean absolute errors (MAEs) of 100 and 112 meV/S relative to experimental formation enthalpies for S^{2-} and S_2^{2-} bearing sulfides in Table I, respectively. With ACFs, the MAEs in the formation enthalpies of the same sets of S^{2-} and S_2^{2-} compounds drop to 98 and 12 meV/S, respectively. Reduction in the MAE of the S_2^{2-} bearing compounds is much larger with the application of ACFs than that in S^{2-} bearing compounds, as expected due to the fact that there are more S^{2-} compounds available in the fitting set and therefore the resulting constant correction for S is numerically closer to the ACF obtained for S^{2-}, and is not as accurate for S_2^{2-}.

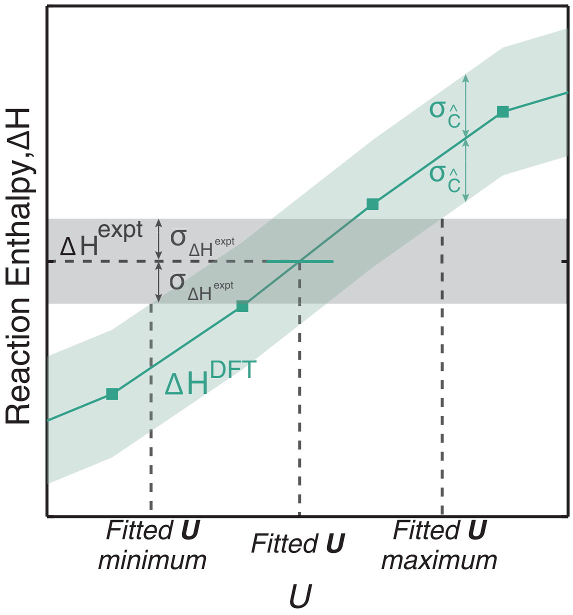

FIG. 1. (Color online) Schematic illustration of the U-fitting process, and how the uncertainties in systematic ACFs ($\sigma_{\hat{C}_i}$) and experimental reaction enthalpies ($\sigma_{\Delta H^{\mathrm{expt}}}$) are taken into account. The $\sigma_{\hat{C}}$ shown in the plot depends on the types of the S anions and their amounts present in the reaction.

Therefore, a single elemental correction factor as commonly employed in previous studies [28,39,40,44] is not sufficient to accurately describe the thermochemistry of all metal sulfides. Moreover, the overall (i.e., considering both S^{2-} and S_2^{2-} bearing compounds) MAE of 103 meV/S is reduced by 25% if the anion-dependent correction factors are applied instead, validating the partitioning of sulfides into groups of S_2^{2-} and S^{2-} bearing compounds and the application of ACFs. We further discuss in Sec. III C how the use of anion-dependent correction factors enables obtaining more reasonable fitted-U parameters.

B. Magnetic structures of *d*- and *f*-block metal sulfides

For all d- and f-block M-S considered in this work, we tested different initial magnetic structures (FM, AFM, ferri, and NM, as described in Sec. II A) at U values between 0 and 8 eV, and report the lowest-energy ones in Fig. 3. We observed that for the compounds which we could find an experimental report on the magnetic structure, that structure is always captured by GGA+U, either at all U or at least in a certain U interval.

C. Thermochemical accuracy of GGA+*U* in *d*- and *f*-metal sulfides redox reactions: Fitted-*U* values and their confidence intervals

The GGA+U sulfurization reaction enthalpies of 15 d- and f-metal sulfide systems are shown as a function of U and compared to the available experimental data in Fig. 4. The corresponding fitted-U values that yield the best agreement with experiments are given in Table III, along with the confidence intervals for these U values obtained from the analysis of experimental and fitting uncertainties as described in Sec. II C. In all d- and f-block metal sulfide systems investigated, we found that the ACFs applied to S anions consistently shift the calculated reaction enthalpies towards the experimental values as shown in a sample case of sulfurization from NiS to NiS_2 as Fig. 5. In this particular example, S anions in the compounds on either side of the reaction are different, while the nominal oxidation state of Ni (i.e., +2) is preserved. As the calculated reaction enthalpy is not considerably sensitive to U, the effect of S corrections is isolated, and we clearly observed that ACFs shift the reaction enthalpy closer to the experimental reaction enthalpy than the constant S corrections, allowing more accurate thermochemical predictions.

The change in the reaction enthalpy with U, on the other hand, is often not systematic, and observed to strongly depend on factors including the chemical identity of metal ion, the type of S anions in the compounds, as well as the type of redox active species in the reaction (i.e., M vs S). The application of U on the metal ion increases the sulfurization reaction

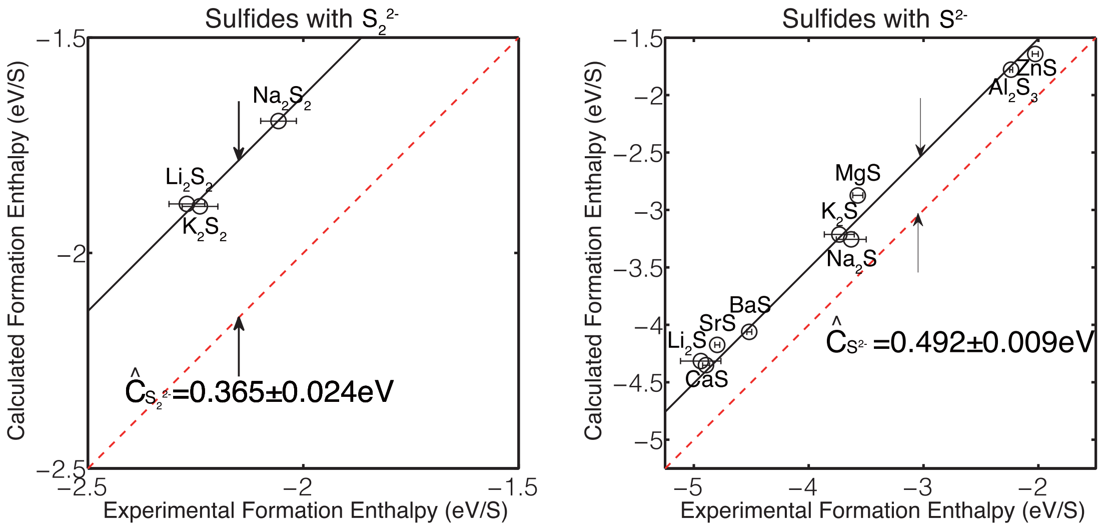

FIG. 2. (Color online) DFT calculated formation enthalpies versus experimental formation enthalpies for simple metal sulfides with S_2^{2-} anion (left) and S^{2-} anion (right).

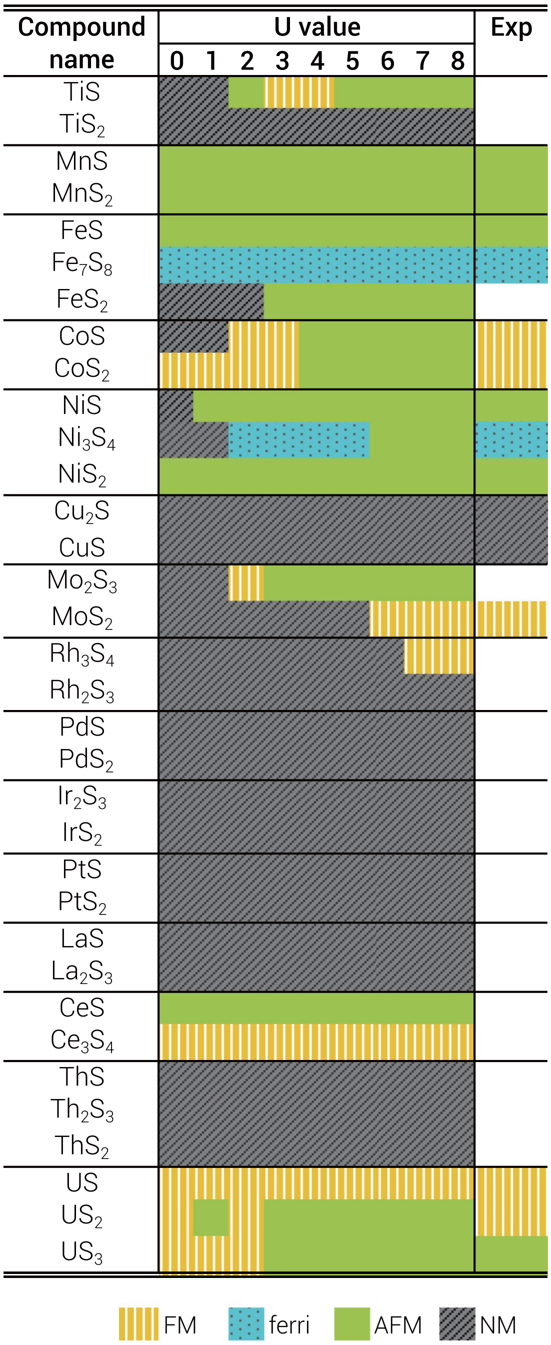

FIG. 3. (Color online) Lowest-energy magnetic structures of d- and f-block metal sulfides investigated in this work as a function of U. Experimental magnetic structures are from Refs. [77,110–124]. Note: For TiS, Mo_2S_3, and US_2 at $U = 2$ eV, ferromagnetic (FM) and antiferromagnetic (AFM) spin arrangements are almost degenerate with energy differences less than 10 meV/f.u.

enthalpy, except several reactions involving Ni, Rh, Th, U, and Ce. We find that when sulfur is the redox active species in a reaction as in the MnS → MnS_2, FeS → FeS_2, CoS → CoS_2, NiS → NiS_2, PdS → PdS_2, the sulfurization reaction enthalpies are less sensitive to U compared to reactions where metal ions perform the redox activity.

For d-metal sulfide systems, GGA ($U = 0$) tends to give more negative sulfurization reaction enthalpies than experimental ranges bounded by uncertainties as shown in Figs. 4(a)–4(k) except for Ti and Rh. GGA+U formation enthalpies are mostly in better agreement with experiments in certain U intervals in d-metal sulfide systems compared to GGA with $U = 0$. However, for most of the f-metal sulfide systems we investigated (except Ce), GGA+U does not provide any clear improvement over GGA.

For most of the systems, as we can see from Table III, even though we have fitted-U parameters, the experimental uncertainties significantly widen the U confidence intervals. For some particular systems such as Ti, Co, Ni, Th, Ce, and U, the large uncertainties and discrepancies in the experimental reaction enthalpies hinder a reliable estimation of U values. For the sulfurization reaction from TiS to TiS_2 in Fig. 4(a), there is a noticeable discrepancy between the experimental data obtained from NBS [67] and Kubascheweski [65] thermochemical tables. The fitted-U interval using the Kubascheweski data ranges from 0 to 4.7 eV centered at 3.7 eV, yet if with the NBS data, the fitted interval shifts to 0–4.0 eV, with two different U values intersecting the experimental enthalpy at 1.4 and 2.8 eV. We later show that among these U values, 1.4 eV gives better cell voltage predictions for the Li/TiS_2 secondary battery system. For the reactions FeS → FeS_2 and Fe_7S_8 → FeS_2 where sulfur is the major redox active species, we obtained fitted-U parameters clustered around 1.4 eV. In contrast, for FeS → Fe_7S_8, a larger U of 4.0 eV is fitted. Similar to testing the performance of multiple U values in Ti-S system, we later show $U = 4.0$ eV yields more accurate Li-battery voltage in Fe-S system.

Overall, there are six M-S systems for which we could not recommend a U value and/or an interval in Table III: Mn, Pd, Ir, La, Th, and U. Among these, the calculated enthalpies of available sulfurization reactions in Mn-S and Ir-S systems get closer to the experimental enthalpy range with increasing U, but do not intersect with the exact enthalpy value within the U value range we tested. Therefore, for these two systems, we provide only a lower bound for the U value. For the reactions in the U-S system, even though we found several intersection points for the calculated and experimental reaction energies at certain U values in Fig. 4(o), we could not recommend a specific U value because the calculated reaction enthalpies are relatively close to or within their experimental reaction enthalpy ranges either at all U or in a wide U range. For the Th-S system, the uncertainties in reaction enthalpies are relatively large, and the calculated enthalpies are not within those uncertainty ranges at any U value we tested, but they are still reasonably close to corresponding experimental reaction enthalpies. There are only two M-S systems with significantly large discrepancies between calculated and experimental reaction enthalpies: Pd-S [Fig. 4(i)] and La-S [Fig. 4(l)], where the experimental reaction enthalpies could not be reproduced with GGA(+U) and ACFs at any U or within any U interval even considering the experimental uncertainties. However, we should note that there are also significant discrepancies between different sources of experimental data for these systems. For example, for PdS, Kubaschewski [65] gives a 298-K formation enthalpy of −70.7 kJ/mol, whereas Zubkov *et al.* [125] reports an enthalpy of −78.1 kJ/mol. These two sets of data result in an approximately 0.1-eV discrepancy in the reaction enthalpy for PdS → PdS_2. Similarly, for LaS,

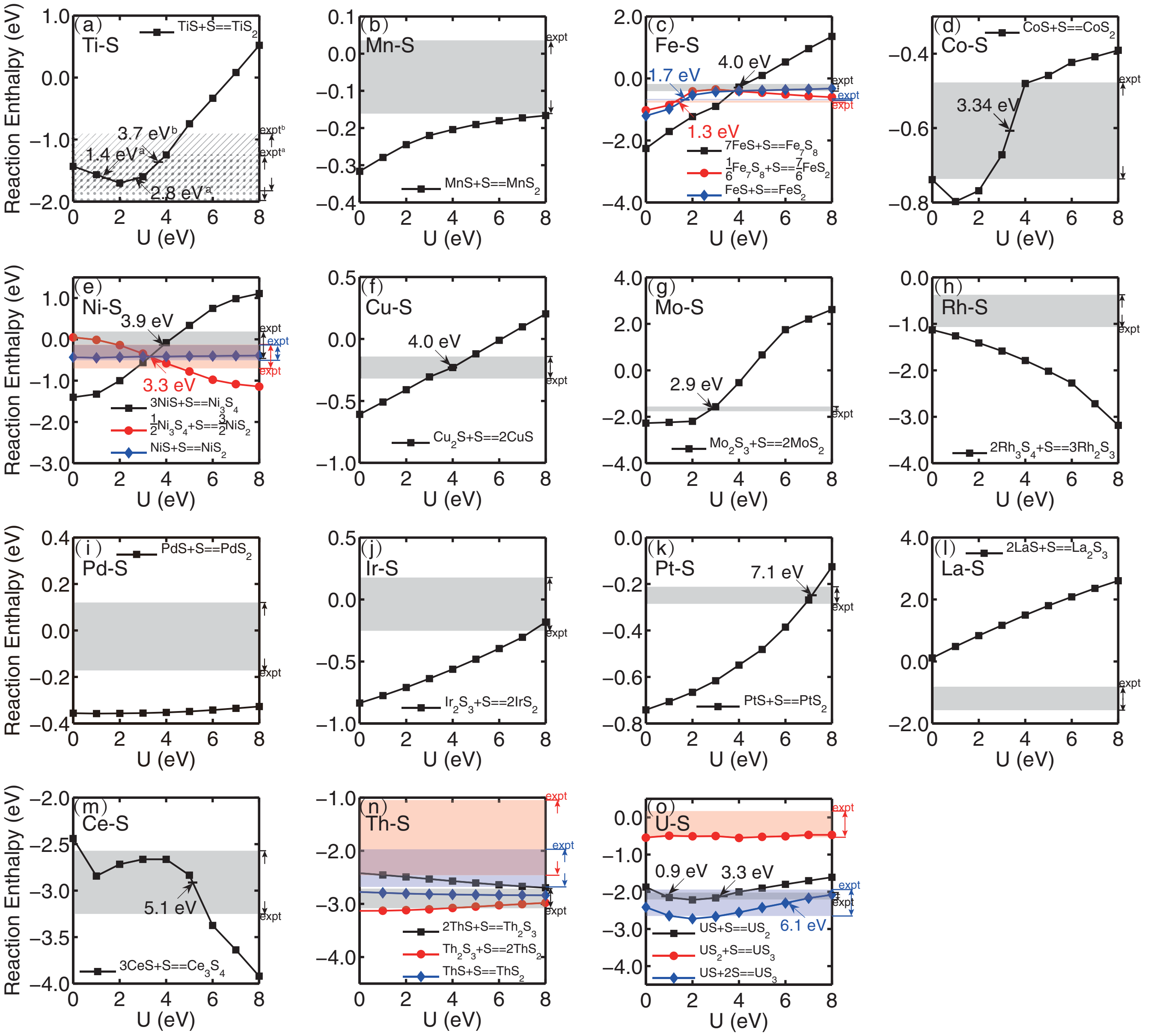

FIG. 4. (Color online) DFT calculated reaction enthalpies ($\Delta H^{\mathrm{DFT}}_{\mathrm{reaction}}$) of the sulfurization reactions as a function of U for d- and f-block metal sulfides of (a) Ti, (b) Mn, (c) Fe, (d) Co, (e) Ni, (f) Cu, (g) Mo, (h) Rh, (i) Pd, (j) Ir, (k) Pt, (l) La, (m) Ce, (n) Th, and (o) U. Experimental reaction enthalpies are shown as bands that cover $\pm\sigma_{\Delta H^{\mathrm{expt}}}$. If obtained, fitted-$U$ values are indicated on plots. For all compounds that appear in the reactions in this figure, we used the lowest-energy state found among the different magnetic configurations evaluated as a function of U in Fig. 3. The standard deviations ($\sigma_{\hat{C}}$) of applied ACFs (see Fig. 1) are not shown for clarity. a and b denote data from the NBS [67] and Kubaschewski [65] tables, respectively.

the Kubaschewski thermochemical database lists a room-temperature formation enthalpy of −472 kJ/mol, whereas the Barin thermochemical database [126] reports −456 kJ/mol. This discrepancy results in an approximately 0.5-eV difference in the experimental reaction enthalpy for LaS → La_2S_3. These discrepancies are on the order of the uncertainties in the experimental reaction enthalpy data, and hinder accurate predictions of U parameters for these systems. Finally, we should emphasize that although we recommend a single, constant U value for a given M-S system in Table III to ensure the total energies of phases calculated will be comparable among all sulfides of M, a single U value may not always accurately represent all oxidation states a metal-ion can access within its compounds [41]. However, the magnitude of uncertainties in experimental enthalpies of sulfides hinders any further analysis to derive local-environment-dependent U values with the method described in Ref. [41].

While the suggested U values in Table III are derived from experimental thermochemical data, we further calculated other physical properties including volumes, magnetic moments, and band gaps of these metal sulfide systems using GGA+U with the suggested U parameters listed in Table III, and compared them to GGA and experimental data in Tables S1, S2, S3 and Fig. S1 in the Supplemental Material [127]. The

TABLE III. Recommended U values and intervals for GGA+U calculations of d- and f-block metal sulfide thermochemistry for Ti, Mn, Fe, Co, Ni, Cu, Mo, Rh, Pd, Ir, Pt, La, Ce, Th, and U, obtained by analyzing the redox reaction energies calculated as a function of U in Fig. 4.

Element	U (eV)	U Interval (eV)
Ti	1.4	[0.0,4.0]
Mn	N/A	>3.1
Fe	4.0	[3.8,4.3]
Co	3.3	[0.0,6.2]
Ni	3.6	[1.2,5.1]
Cu	4.0	[2.6 5.1]
Mo	2.9	[2.7,3.0]
Rh	0[a]	0[a]
Pd	N/A	N/A
Ir	N/A	>7.1
Pt	7.1	[6.8,7.5]
La	N/A	N/A
Ce	5.1	[0.3,5.8]
Th	N/A	N/A
U	N/A	N/A

[a] Estimated based on the assumption that the smallest U that can be applied is 0 eV.

analysis in Fig. S1 shows that GGA and GGA+U both yield reasonable volume predictions for most of the systems except for FeS_2, where $U = 4$ eV results in an unacceptable deviation of 38% from the experimental volume and therefore this thermochemical U parameter should be applied with caution in this system especially in nonthermochemical property investigations. GGA and GGA+U yield similar standard deviations of around 1.2 Å^3/atom from experiments, but similar to previous reports in metal oxides [41,128], GGA+U tends to overestimate the crystal volumes more than GGA. Magnetic moments in Table S2 show for the limited number of available experimental data [119,122,129] to compare, GGA+U improves the magnetic moments predictions over GGA. GGA is well known to underestimate the band gaps, and GGA+U even with the U parameters fitted to the thermochemical data mostly improves the band-gap predictions in metal sulfides with respect to experimental data [130] (Table S3). Overall, GGA+U with U values derived for thermodynamic prediction yields reasonable predictions for physical properties (volumes, magnetic moments, and band gaps) for most of the metal sulfides considered in this work.

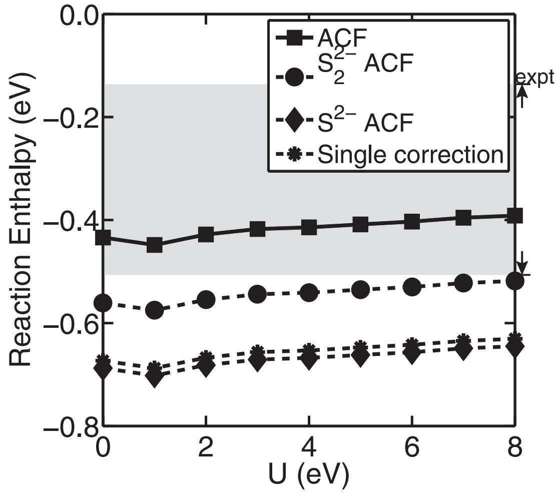

FIG. 5. Comparison of applying different correction factors for sulfurization reaction $NiS + S \rightarrow NiS_2$ including anion-dependent correction factors (ACFs), a constant ACF for S_2^{2-} (i.e., 0.365 eV/S) and S^{2-} (i.e., 0.492 eV/S), respectively, and a single, constant Wang *et al.* [39] type correction (i.e., 0.477 eV/S) by fitting to all simple metal sulfides included in Table I without partitioning with regard to sulfur anion type.

D. Applications in prediction of M-S battery voltages

In this section, we investigate the performance of the fitted-U values and ACFs in predicting experimental battery voltages for a wide spectrum of M-S battery systems including Li/TiS_2, Li/FeS_2, Li/Mo_6S_8, and Mg/Mo_6S_8 systems. For a given discharge reaction: $A_mX + nA \rightarrow A_{m+n}X$, where A represents the insertion ion and X denotes the intercalation host, the average battery discharge voltage between these two compositions can be computed as

$$V = -\frac{E^{\mathrm{DFT}}_{A_{m+n}X} - E^{\mathrm{DFT}}_{A_mX} - nE^{\mathrm{DFT}}_{A}}{nke}. \tag{10}$$

Here, k denotes the valence of the inserting ion A, nk is the total number of electrons transferred in the reaction, and E_p^{DFT} denotes the DFT calculated total energy of compound p in eV.

For the Ti and Fe systems, there is more than one U value obtained in Sec. III C, so we first evaluated which of those values yield more accurate voltage predictions in these systems. The fitted-U parameters for Ti from Sec. III C are 1.4, 2.8, and 3.7 eV, and the calculated battery cell voltages using those U values for the full lithiation of Li/TiS_2 cell are 2.26, 2.43, and 2.54 V, respectively. Comparing with an experimental discharge voltage of 2.18 V [131], we found that $U = 1.4$ eV yields more accurate calculations in the Ti-S system. For the Fe-S system, the fitted U values are 1.4 and 4.0 eV. Using these two different U values for Fe, we calculated the voltage as 1.65 and 2.02 V, respectively, for the complete lithiation of FeS_2. Since the experimental report of the voltage is 2.20 V [132], we conclude that a U value of 4.0 eV can provide more accurate thermochemical predictions in the Fe-S system.

Using the U values selected for Fe and Ti as described above, and using the recommended U value for Mo (Table III), we compare the voltages calculated for a series of discharge reactions in TiS_2, FeS_2, and Mo_6S_8 cathode systems with and without ACFs and +U in Table IV. We found that except for TiS_2 voltage, the GGA+U+ACF scheme significantly improves the agreement between the calculated and experimental voltages in all systems. The most substantial improvement in the accuracy of voltage prediction with the GGA+U+ACF is achieved in the FeS_2 battery system. In the discharge reaction $FeS_2 + 2Li \rightarrow Li_2FeS_2$, the $^-$S–S$^-$ covalent bond breaks according to the bond distance analysis outlined in Sec. II C, in agreement with previous experimental studies [133,134]. Thus, we need to apply different ACFs to the GGA+U calcu-

TABLE IV. Comparison of GGA calculated cell voltages with and without anion-dependent systematic error correction factors (ACFs) and U parameters applied with experimental cell voltages of Li/TiS_2, Li/FeS_2, Li/Mo_6S_8, and Mg/Mo_6S_8. APE denotes the absolute percent error relative to the experimental voltage.

Discharge reaction	Experimental voltage (V)	Calculated voltage (V)			
		GGA ($U = 0$)	APE (%)	GGA+U+ACF	APE (%)
$TiS_2 + Li = LiTiS_2$	2.18 (Ref. [131])	2.09	4.2	2.26	3.4
$FeS_2 + 2Li = Li_2FeS_2$	2.20 (Ref. [132])	1.18	46.5	2.02	8.4
$Mo_6S_8 + Li = LiMo_6S_8$	2.39 (Ref. [135])	1.96	18.0	2.11	11.8
$LiMo_6S_8 + 3Li = Li_4Mo_6S_8$	1.92 (Ref. [135])	1.74	9.2	1.86	3.0
$Mo_6S_8 + 4Li = Li_4Mo_6S_8$	2.04 (Ref. [135])	1.79	11.8	1.92	5.6
$Mo_6S_8 + Mg = MgMo_6S_8$	1.38 (Ref. [136])	0.99	28.0	1.10	20.3
$MgMo_6S_8 + Mg = Mg_2Mo_6S_8$	1.09 (Ref. [136])	0.84	23.5	0.97	11.7
$Mo_6S_8 + 2Mg = Mg_2Mo_6S_8$	1.24 (Ref. [136])	0.91	26.1	1.03	16.5

lated energies of FeS_2 and Li_2FeS_2. For this particular system, GGA induced absolute percent error (APE) relative to experiment for the discharge reaction above is 47%, and GGA+U alone can reduce this APE to 16%. The application of ACFs provides a further improvement in accuracy (with an 8% reduction), and the overall APE of GGA+U+ACF method is 8%, which is a significant improvement over uncorrected GGA.

For the other battery reactions based on Ti-S and Mo-S systems, since sulfur anions do not transition from S^{2-} to S_2^{2-} in the discharge reaction, the same ACF is applied to A_mX and $A_{m+n}X$ and therefore the improvement of calculated voltages depends solely on applied U values. While for the Ti-S reaction, improvement in predicted voltage with GGA+U relative to GGA is only marginal, voltages of reactions pertaining to Mo_6S_8 cathode are all significantly and systematically improved compared to GGA. Overall, the mean absolute percent error (MAPE) of all reactions in Table IV drops from 21% to 10% by applying U and ACFs, relative to standard, uncorrected GGA.

IV. CONCLUSIONS

This work assesses the relative accuracies of GGA and GGA+U predictions in the reaction thermochemistry of 24 M-S systems including M = Li, Na, K, Mg, Ca, Sr, Ba, Zn, Al, Ti, Mn, Fe, Co, Ni, Cu, Mo, Rh, Pd, Ir, Pt, La, Ce, Th, and U. Based on previous studies [39,40], the inaccurate thermochemical predictions in M-S systems using standard, uncorrected GGA calculations can be attributed to two major sources: a systematic error that can be associated with the anion (e.g., O, F, etc.) and the self-interaction error. Different from O^{2-} in oxides and F^- in fluorides, sulfur anions in M-S can exist in two common states, namely, S^{2-} and S_2^{2-}, resulting in different bond characteristics and therefore different levels of systematic error cancellation in DFT redox thermochemistry. Thus, the systematic error for M-S systems can be consistently mitigated by fitting anion-dependent correction factors (ACF) for S anions using the experimental formation enthalpies of simple metal sulfides that are partitioned with regard to the sulfur anion type. Compared to using a single, constant correction factor, the application of ACF reduces the MAE of DFT predicted formation enthalpy of simple metal sulfides by around 25%. The self-interaction error, on the other hand, has been remedied by a constant U-fitting scheme in 15 d- and f-block metal sulfide systems. Based on the experimental formation enthalpies, we have predicted effective thermochemical U parameters for the d- or f-metal ion in each M-S system. We observed that variation of the sulfurization reaction enthalpies as a function of U applied on the metal ion does not follow a consistent trend across the periodic table and strongly depends on the chemical identity of the d- and f-block metal ions, anion type of sulfur in M-S, and the redox active species (metal versus sulfur) as well as the magnetic structures of the compounds. Moreover, we have further demonstrated that by combining ACF and GGA+U with U parameters suggested in Table III, we are able to improve DFT predictions on cell voltage of M-S based battery systems including Li/FeS_2, Li/TiS_2, Li/Mo_6S_8, and Mg/Mo_6S_8. Compared to uncorrected GGA, ACF and GGA+U reaches an overall average reduction from 21% to 10% of mean absolute percent error (MAPE) relative to experimental voltage data.

In the analysis of M-S thermochemistry within the GGA+U+ACF framework, we fully took into account the uncertainties in the experimental formation enthalpies, both during the evaluation of ACFs for S anions in simple metal sulfide formation reactions with GGA, and redox reactions of d- and f-metal sulfides with GGA/GGA+U. Since simple metal sulfides have small experimental uncertainties, we have obtained ACFs with low variances and tight confidence intervals. However, we showed that compared to previously studied systems such as d-metal oxides systems, discrepancies and larger uncertainties in experimental enthalpies of d- and f-block metal sulfides hinder an accurate prediction of effective U parameters in almost all M-S systems, and broaden their confidence intervals. This observation not only calls for more accurate experimental enthalpy measurements for d- and f-metal sulfide systems, but also indicates that incorporation of uncertainties into analysis is essential while assessing the accuracy of DFT calculations in systems with large reported uncertainties in experimental formation enthalpies, such as metal halides and phosphides.

As a final remark, the framework we present based on the anion-dependent correction for S anions and its combination with the GGA+U method builds on the previously suggested methods focusing on improving DFT accuracy in predicting thermochemical properties [39–44]. These previous approaches fitted a single correction factor for each elemental reference state using compound formation reactions, with differences in subsets of compounds included in fitting and/or U values used. In the ACF approach, we assigned the correction to the anion rather than the elemental reference, so as to allow the application of different corrections in reactions where S goes from elemental S to different anion states in compounds. Based on GGA and GGA+U, this framework employs a semiempirical approach to improve the accuracy of thermochemical predictions for metal sulfides, and requires fitting chemical-identity-specific parameters. Hybrid functionals (such as HSE06, PBE0, and B3LYP) may provide accurate thermochemical predictions without such corrections, but according to previous analyses in similar transition-metal systems [128,137,138], the improvement in the accuracy of redox reaction energies with hybrid functionals over GGA is almost numerically similar to that obtained with GGA+U. More importantly, hybrid functionals are computationally expensive compared to GGA(+U) [128,137] and are currently impractical to implement in the state-of-the-art high-throughput DFT frameworks. The implementation of our GGA(+U) methodology into high-throughput DFT frameworks is straightforward, and only requires accurate partitioning of anions in compounds, such as differentiating S^{2-} and S_2^{2-} as outlined in Sec. II C, upon fitting the chemical potential corrections.

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