Formation energies from DFT calculations

Formation energies calculated using standard density functional theory are known to contain significant systemic errors. For example, those of many binary oxides are under-predicted due to the over-binding of molecular oxygen (using local/semi local functionals),\textsuperscript{1,2} which can be corrected by apply an rigid shift of the energy for the latter. For transition metal binary oxides, additional errors arise from the localised d-electrons which need to be treated with Hubbard-correction, and the U value may be fitted to the relative formation energy.\textsuperscript{3}
However, energies GGA+U calculations cannot be mixed with those from GGA calculations since they are on different levels of theory. One scheme was proposed to allow mixing of the entries by applying another rigid energy shift ($\Delta E_M$) to the GGA+U energies scaled with the number metal atoms where the U is applied to. This allows the Hubbard correction to be used only in environments that they are most applicable, such as oxides and fluorides. The two corrections mentioned above are used by the Materials Project where the Hubbard correction is only applied to oxides and fluorides of transition metals, and standard GGA calculations are used for sulphides. A slightly different approach is used by the Open Quantum Materials Database, where the GGA+U is used for all materials containing the transition metals, with the elemental formation adjusted to fit the experimental formation energies.

In this work, we are mainly concerned about the stability of oxysulphides, where the competing phases are going to be the binary/ternary oxides and sulphides. We apply the Hubbard+U correction to the oxysulphides because Fe ions are expected to be in the +2 or +3 oxidation states, and the Hubbard correction is used for the sulphides as well. In contrast, the Materials Project’s approach computes the competing FeS and FeS$_2$ phases using GGA. To evaluate different schemes, the reaction energies of several reactions are computed and compared with the values obtained using experimental formation energies obtained from the Kubaschewski Table. The differences between the theoretical and the experimental values are shown in Figure S1, where All refers to the scheme where GGA+U is used for all species, and Oxide only is calculated using GGA for sulphides and with corrections applied to oxides. The MP-ORIG refers to the data extracted directly from the Materials Project with their corrections applied. The Oxide only is refitted using the methodology that MP-ORIG refers to, as we are not able to reproduce the fitting of corrections for the latter ($U = 5.3$ eV, $\Delta E_M = -2.733$ eV). Interestingly, our refitted U and the $\Delta E_M$ terms are very close to the ones reported in the two methodology papers. Recently, a revised correction scheme was proposed using the data from the NIST-JANAF table give similar results with negligible differences.
proposed by the Materials Project group and made available online. The results obtained using this scheme is labelled as MP-2020 (U = 5.3 eV, $\Delta E_M = -2.256$ eV). One should note that here the newer PBE PAW data set is used with Fe$_{pv}$ for Fe, Li$_{sv}$ for Li, O for O and S for S. The two papers mentioned above did not report the exact pseudopotential version that was used. The Materials Project also uses the Fe$_{pv}$ potential, from an older pseudopotential set PBE.

The reaction FeS + Li$_2$S $\rightarrow$ FeO + Li$_2$O can be used as benchmark for the treatment of sulphides, as it does not contain any elemental phases so the errors involved there would have no effect. Assuming that most of the DFT errors come from the treatment of the Fe, having an formation energy that is too negative means that the oxides are overly favoured, and vice versa. As shown in Figure S1, using U for both oxides and sulphides makes FeO slightly favoured (the All scheme), whereas if it is only applied to the oxides, the FeS is more favoured. If one assumes that the $\Delta E_M$ correction for mixing GGA/GGA+U is sufficient for oxides, this implies that the standard GGA calculation favours FeS and its energy is predicted to be lower. The same behaviour is found in oxides using plain GGA, where the errors from overly localised the d electrons are found to compensate some of that from the oxygen over-binding. The error from the original Material Project scheme (MP-ORIG) for this particular reaction may appear to be small, but it is for the wrong reason as two other oxide/sulphide exchange reactions gives very large errors. In fact, the data from the Materials Project appear to be incorrectly calibrated for reproducing the reaction energy of oxidizing FeO to Fe$_2$O$_3$ and Fe$_3$O$_4$ (shown in the Fitting U for Fe of Figure S1), nor does it reproduces the binary formation energies of iron oxides (shown in the GGA+U/GGA Mixing of Figure S1). The new material project corrections (MP-2020) appears to be correctly calibrated to the binary oxide formation energies with a revised $\Delta E_M$, but it suffers from the same problem for the reaction energies of oxidising FeO, due to the inconsistent $U_{Fe}$ calibration. On the other hand, both two sets of reaction energies are well reproduced by the Oxide only data, which is not a surprise, since it was to calibrated to reproduce them. The All scheme
does not include the $\Delta E_M$ term and hence is not expect to give accurate formation energies for iron oxides, but we are only interested in the competition between the quaternary and binary phases here so including this extra term has no effect. Hence, the All scheme is most suitable for investigating the stabilities of the oxysulphides.

**Gibbs’s free energy at finite temperature using machined learned descriptors**

The energies from the DFT calculations can only be used to access the thermodynamic stability at 0 K. At finite temperature, the synthesisbility of a material depends on its Gibbs’s free energy, but the incorporation of temperature effects is not trivial using first-principles calculations. The vibrational entropy may be accounted for using phonon density of states under the quasi-harmonic approximation, which can be very resource intensive. Recently, a machine learning model for estimating the Gibbs’s free energy has been reported. In that work, it was found that the Gibbs energy may be estimated to a good accuracy using the enthalpy given by DFT plus an additional analytical term that is data mined using the sure independence screening and sparsifying operator (SISSO) method. This additional term takes only takes the composition of the material, the volume of the DFT relaxed structures, and the temperature as the input.

Applying this approach allows us to estimate the synthesisbility at finite temperature. The results are plotted in the Figure S2. It is found that the phases that are predicted to be close to the convex hull remain close at finite temperatures. Interestingly, the number of stable phases appear to increase with increasing temperature. This is reflected in both the computed distance to hull as well as the distance to hull formed by the known non-quaternary phases.

However, we note that these results under finite temperatures can have several caveats. First, the contribution of configurational entropy is not explicitly included, which could make
disordered phases more favourable at high temperatures, and one example is the Li$_2$FeSO. Second, the physical descriptor was fitted using the Materials Project’s data, which are computed using a similar but not identical pseudopotential set. In addition, the U for Fe d electron is 4 eV here whereas the Materials Project uses 5.3 eV. This could result in inconsistency in the both the energy of Fe-containing phases and their equilibrium volumes. Second, the training and testing set of the descriptor only includes the known experimental phases, whereas here we are applying it to a large set of newly predicted structures. During the search, many metastable phases that have higher volume per atom are found, which would have much reduced $G_{SISSO}^{\delta}$ term due to its volume dependency. In some cases, predicted phases that are more than 100 meV above the hull at 0K can be stabilised. Since such hypothetical structures are clearly not included in the training set, and the model is essentially being extrapolated, making it less reliable. Hence, we have limited the phase considered in Figure S2 to those having the lowest energy at 0 K for each composition. Finally, it should be noted that the descriptor was shown to have a Mean Absolute Error (MAE) of 46 meV, which is not negligible although some of the error cancellations are expected as we are limited to four elements here.

**Data availability**

The structure searching results, raw calculation data for phonon, neb and hybrid functional calculations, an archive containing the provenance of all calculations for the AiiDA framework, and example notebooks for data analysis and plotting have been deposited into the Zenodo repository with open access. DOI: [10.5281/zenodo.4977232](10.5281/zenodo.4977232).
Fig. S1: Errors in the reaction energy using different schemes for treating Fe-containing oxides and sulphides with Hubbard correction. The All scheme uses $U_{Fe} = 4.0\text{eV}$ for both oxide and sulphides. The Oxide only uses the $U_{Fe} = 4.0\text{eV}$ for oxides but not for sulphides, and the GGA+U energies are corrected by a $\Delta E_M$ term (1.787 eV) so it can be mixed with the GGA calculations. The MP scheme uses the same methodology as the Oxide only, but the energies are obtained directly through the Materials Project API using their settings and corrections ($U_{Fe} = 5.3\text{eV}$, and $\Delta E_M = 2.733$).
Fig. S2: Finite temperature stabilities predicted using the physical descriptors data mined by the SISSO method. It can be seen that the stabilities of most phases does not change much with temperature, but there are exceptions.
Fig. S3: (a) The ordered $Li_2FeSO$ structure reported previously. (b) The mode-pushed structure with $a^-b^-c^0$ tilted octahedra. (c) The phonon band structure of the order $Li_2FeSO$ with imaginary frequencies. (d) The phonon band structure of the mode-pushed structure without any imaginary frequency. Colour coding: cream-S, purple-Li, cyan-Fe, pink-O.
Fig. S4: Phonon dispersions calculated for (a) Li$_2$FeSO, (b) Li$_4$Fe$_3$S$_3$O$_2$, (c,d) Li$_2$Fe$_3$S$_2$O$_2$ and (e,f) Li$_2$Fe$_4$S$_3$O$_2$
Fig. S5: Projected density of states for predicted phases computed using HSE06 hybrid exchange. The valance band tops are consisted of Fe d states, O p states and S p states, and the conduction band maximum is dominated by Fe d states. The band gaps of these materials are about 2 eV.
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