Phase Equilibria in the U-Si System from First-Principles Calculations

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Abstract

Density functional theory calculations have been used with spin-orbit coupling and on-site Coulomb correction (GGA+ U) methods to investigate the U-Si system. Structural prediction methods were employed to identify alternate stable structures. Convex hulls of the U-Si system were constructed for each of the methods to highlight the competing energetics of various phases. For GGA calculations, new structures are predicted to be dynamically stable, but these have not been experimentally observed. When the GGA+ U ($U_{eff} > 1.3$ eV) method is considered, the experimentally observed structures are predicted to be energetically preferred. Phonon calculations were used to investigate the energy predictions and showed that the use of the GGA+ U method removes the significant imaginary frequencies observed for U_3Si_2 when the correction is not considered. Total and partial electron density of states calculations were also

performed to understand the role of GGA+ U methods and orbitals on the bonding and stability of U-Si compounds.

1. Introduction

Uranium silicide compounds have received great interest recently as a potential replacement for uranium dioxide fuel in commercial light water reactors (LWRs) [1]. In particular, U_3Si and U_3Si_2 are seen as attractive candidates due to their higher uranium density, allowing the option of a leaner core with fewer assemblies, a lower enrichment fuel or an extended lifetime of a fueled core. In addition, improved thermal conductivity and heat capacity relative to UO_2 can result in a cooler pellet with less stored energy providing added accident tolerance during scenarios such as a loss of coolant or reactivity insertion accidents [2,3]. A number of issues have been identified that may influence the employment of U_3Si , such as runaway swelling and rapid amorphization at low temperatures and low irradiation doses [4-8].

Work on U_3Si_2 -Al dispersion fuels [9-11] and UN- U_3Si_2 composites [12] suggest that U_3Si_2 may be a viable option for LWRs as compared to U_3Si . A number of recent efforts have shown U_3Si_2 may be manufactured via methods such as powder metallurgy [13], ball milling [14] and arc melting [15,16]. White and co-workers have extensively studied the thermophysical properties of U_3Si_2 and other uranium silicide compounds [16-19]. The thermal expansion, heat capacity and thermal conductivity of U_3Si_2 are reported [16], which will contribute to LWR fuel design. Improvements to the manufacturing

procedure is still a work in progress, as the resulting U_3Si_2 samples are often Si-lean and contain small amounts of secondary phases [15,16], while efforts to improve to the cost of manufacture also need to be explored.

The tetragonal structure of U_3Si_2 with space group $P4/mbm$ was first reported by Zachariasen [20] and later confirmed by Remschnig *et al.* [21]. Since Zachariasen's work, numerous binary and ternary compounds with this U_3Si_2 -prototype structure have been reported as noted in the review by Lukachuk and Pöttgen [22]. Within the actinide series, Th_3Si_2 [23], Np_3Si_2 [24] and Pu_3Si_2 [25] are reported as isostructural with U_3Si_2 . Zachariasen [20] originally reported that USi adopts the FeB-type structure. However, the FeB-type structure is believed to be stabilized by oxygen [26]. The currently accepted structure for the USi phase is reported as off-stoichiometric $\text{U}_{68}\text{Si}_{69}$ [26].

Given the potential importance of the U-Si system, it is critical to have an understanding of its phase equilibria before employment in a commercial reactor. Phase equilibria form the foundation upon which to explore fuel performance related properties such as thermal conductivity/heat capacity, radiation damage effects or fission product behavior. Computational modeling provides an avenue to investigate the aforementioned phenomena. Existing theoretical work has investigated a select set of the phases identified in experiments [27-29]. Yang *et al.* [27] and Yagoubi *et al.* [29] reported the structural and elastic properties of many U-Si compounds, but did not include results for U_3Si_2 . Wang *et al.* reported the structural, elastic properties and point defect energetics of U_3Si_2 [28]. However, none of these studies have explored any of the alternative phases identified in the present study and thus did not fully appreciate the complexity of the phase diagram caused by the competition between different phases or how this competition relates to the properties of the uranium *5f* electrons.

We present first-principles calculations within the density functional theory (DFT) framework [30,31] using several different methods and two different software packages to explore the various phases in this system. Historically, this comprehensive approach to analyzing the complicated nature of the *5f* electrons in uranium-containing phases has resulted in successful descriptions of uranium-based compounds [32-35]. In this work, we used a structure predictor algorithm to search for candidate ground-state structures at various fixed compositions in the U-Si system. This allowed us to readily explore composition space in the regions of interest. Our results reveal two previously unreported structures for the U-Si system. These structures, at compositions of USi and U_2Si , are likely to be a result of the methodology used as neither has been observed experimentally. The energetics of all U-Si phases are sensitive to the methodology used to describe the uranium *5f* electrons, which is explored by systematically varying the Hubbard *U* parameter in the GGA+*U* method. This study provides understanding of how

the experimental USi and U₃Si₂ structures are recovered as the thermodynamic ground state for Hubbard U values above a critical value, which has not been previously recognized.

2. Computational Details

Initial DFT calculations use the Vienna *ab initio* Simulation Package (VASP) [36-38]. The projected augmented wave (PAW) method [39,40] within the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [41] is employed. For accurate structural relaxations, the plane-wave energy cutoff is set to 500 eV along with a 0.125 eV smearing of the partial occupancies in the Methfessel-Paxton method [42]. The Brillouin zone (BZ) was sampled with Monkhorst-Pack (MP) meshes [43] chosen such that the total energy converged within 1 meV.

Additional DFT calculations are performed with the full-potential linearized augmented plane-wave (FP-LAPW) method using the WIEN2k software [44]. The GGA-PBE scheme for the exchange-correlation potential is used. The atomic sphere radii, R_{MT} , is set to 2.4 bohr and 2.1 bohr for U and Si, respectively. The basis sets for well-converged calculations use the parameters $R_{mt} \cdot K_{max} = 9$, $G_{max} = 25 \text{ Ry}^{1/2}$, and $L_{max} = 10$. The number of k -points in the full Brillouin zone was chosen to be sufficiently large for energy convergence. Fully-relativistic calculations for spin-orbit (SO) coupling was included using the second variational approach, in which relativistic $p_{1/2}$ local orbitals are added to the uranium atoms [45,46].

The GGA+ U method is used to explore the effect of orbital dependent potentials, which are applied to the $5f$ states in uranium [47,48] to capture their correlated nature. The implementation of GGA+ U applied here is rotationally invariant, meaning that an “effective” $U_{eff} = (U - J)$ is used, where J is set to zero. The value of U_{eff} may be chosen from spectroscopy data or inferred from experimental data such as lattice constants or bulk modulus. One study used X-ray photoemission spectra (XPS) to probe the bandwidths in uranium silicides, but an appropriate value for U_{eff} cannot be inferred from the data [49]. Thus, U_{eff} is treated as a fitting parameter in the current set of calculations. Although GGA+ U may lead to metastable electronic structure solutions, we find this effect to be quite small: the enthalpy difference for a GGA+ U calculation ($U_{eff} = 1.5 \text{ eV}$) for U₃Si₂ with and without the U -ramping method [50] is about 0.01 eV/atom.

Structure prediction calculations are performed with the particle swarm optimization method in CALYPSO [51,52]. Unit cell sizes up to four formula units are searched for

the following fixed compositions: USi, U₃Si₂ and U₂Si. The structural energies are calculated using VASP for GGA and GGA+*U*. Searches using GGA+*U* with $U_{\text{eff}} = 0.5$ eV yield the same structures as GGA. Additional work with $U_{\text{eff}} = 1.0, 1.5$ eV and 2.0 eV did not yield additional structures with enthalpy lower than the experimental structures. The reported structural symmetry and Wyckoff positions are from FINDSYM [53].

Structure searches for USi and U₃Si₂ compounds using GGA found different structures than the experimentally known USi FeB-type and U₃Si₂-prototype. To avoid confusion, we have adopted a nomenclature where the space group is affixed to the composition in order to distinguish structures. Thus, USi FeB-type and U₃Si₂-prototype will be denoted as USi-*Pnma* and U₃Si₂-*P4/mbm*, respectively. The new structures at these compositions are given as USi-*Imma* and U₃Si₂-P1. We report only the ground-state structure for other compositions. Namely, U₃Si (space group *Fmmm*) [54], U₂Si (new type), β -USi₂ (AlB₂-type) and USi₃ (AuCu₃-type).

Structures with low enthalpy are checked for dynamic stability using VASP. The phonon dispersion curves are calculated using the two different methods implemented in the PHONOPY software [55]. Force constants are calculated via the finite displacement method [56] and density functional perturbation theory (DFPT) [57], which should lead to the same solutions. However, we find that force convergence for ferromagnetic phases is difficult to achieve when using the finite displacement method. Moreover, since each finite displacement calculation starts from scratch with no knowledge of the ground state wave function, it is possible that even small variations due to a metastable solution can lead to issues with phonon predictions. This problem is avoided in the DFPT approach, because the forces of the perturbed structures are calculated based on the wave function of the ground state structure. Thus, DFPT is used when calculating force constants for ferromagnetic USi-*Pnma* and U₃Si₂-*P4/mbm* while the finite displacement method is used for non-magnetic U₂Si, U₃Si₂-P1 and USi-*Imma*. If the finite displacement calculations are performed using the ground state wave function as the starting point, the results agree well with the DFPT calculations. All calculations used $2 \times 2 \times 2$ supercells. The Monkhorst-Pack meshes for U₂Si, U₃Si₂-*P4/mbm*, U₃Si₂-P1, USi-*Imma*, and USi-*Pnma* are $5 \times 5 \times 5$, $2 \times 2 \times 4$, $3 \times 3 \times 3$, $7 \times 7 \times 7$ and $2 \times 2 \times 4$, respectively. The high symmetry paths in reciprocal space are determined with AFLOW online [58,59].

The elastic constants experienced similar convergence difficulties. Here, the elastic constants for non-magnetic phases are calculated using a stress-strain method with an applied strain of 10^{-4} using VASP to calculate the forces [60]. In this method, all the stress components are coupled to the elastic constants, which enables calculation of elastic properties for any crystal symmetry. For U₃Si₂-*P4/mbm*, we used the stress-strain

method implemented in VASP [61,62]. Since the latter methodology avoids a complete restart with a new wave function, as compared to the ground state, any issues related to metastable solutions are minimized, similar to the phonon calculations.

In summary, we search for candidate U-Si compounds using CALYPSO with VASP as the DFT engine. The construction of the convex hull is critically important in determining whether a compound has a low enthalpy in relation to other competing compounds. The DFT description used for bonding (e.g., GGA or GGA+ U) will change which compounds are on the convex hull, as demonstrated in the results. We use WIEN2k as a means to explore any possible effect of semi-core electrons on bonding. Since structural optimization in WIEN2k is quite an extensive task for low-symmetry structures, we optimize the volume only by fitting the data to a Birch-Murnaghan equation of state. Thus, the lowest enthalpy found here cannot be guaranteed to be the global minimum, but the reported enthalpy of formation values should still provide an accurate construction of the convex hull.

3. Results and Discussion

3.1 Convex Hull

The experimental U-Si phase diagram [63] includes several slightly non-stoichiometric phases derived from the USi_2 parent lattice, which in itself is believed to be metastable. The AlB_2 -type and ThSi_2 -type structures form the lattices for the U_3Si_5 and $\text{USi}_{1.88}$ phases, respectively [21]. (Exploration of the structural and thermodynamic properties of these phases, however, is outside of the scope of this work.) This implies that the true convex hull is going to differ slightly from what is reported here. However, our calculations suggest that this slight difference in composition for these Si-rich phases (U_3Si_5 and $\text{USi}_{1.88}$) will not change the analysis relating to the stability for the uranium-rich phases of interest because the shape of the convex hull will not be greatly altered.

The convex hull showing the compounds with the lowest enthalpy relative to Si and α -U for GGA and GGA+SO calculations is shown in Figure 1. Table 1 gives the relevant structural parameters. The enthalpy values for GGA calculations are reported using both VASP and WIEN2k. As these are quite similar, the enthalpy values for GGA+SO are only reported for WIEN2k. Five compositions are on the hull for GGA+SO: USi_3 , USi_2 , USi-Imma , U_2Si and U_3Si . The importance of including spin-orbit coupling is noted by USi_2 , which is on the convex hull for GGA+SO, but not GGA calculations. The enthalpy of USi_2 drops 0.07 eV/atom when spin-orbit coupling is included, but the effect is much

less for other compounds (~ 0.01 eV/atom). This may be due to USi_2 being ferromagnetic with a total magnetic moment of $1.3 \mu_B$ per uranium atom, while the other compounds are non-magnetic.

The USi-Imma and U_2Si structures have not been reported previously. USi-Imma is orthorhombic with c/a (2.30) and c/b (2.28) ratios that resemble the c/a ratio of 2.30 for the experimentally reported $\text{U}_{68}\text{Si}_{69}$ tetragonal structure [26]. The U_2Si structure is monoclinic and has no known analogue in other actinide-silicide compounds. For USi-Imma and U_2Si , spin-orbit coupling has little effect on the energetics and these phases are on the convex hull for both GGA and GGA+SO calculations.

No U_3Si_2 structures are on the convex hull for GGA or GGA+SO meaning that the method predicts this stoichiometry to be unstable. The $\text{U}_3\text{Si}_2\text{-P4}/mbm$ structure is ferromagnetic with a magnetic moment of $1.3 \mu_B$ per uranium atom (GGA+SO). Experimental measurements exhibit temperature dependent paramagnetism down to 2 K, but a different magnetic behavior at 0 K cannot be ruled out [21]. The $\text{U}_3\text{Si}_2\text{-P4}/mbm$ enthalpy of formation is above the convex hull by 0.17 and 0.10 eV/atom for GGA and GGA+SO calculations, respectively. This signifies that, like USi_2 , spin-orbit coupling has a significant effect on the formation enthalpy. In contrast, $\text{U}_3\text{Si}_2\text{-P1}$ is non-magnetic with an enthalpy of formation that is 0.01 eV/atom above the hull formed by USi-Imma and U_2Si for GGA+SO calculations.

Calculations using GGA+ U +SO show that increasing U_{eff} changes which compounds are on the convex hull and is especially relevant for the $\text{U}_3\text{Si}_2\text{-P4}/mbm$ structure, which is stabilized relative to the non-magnetic $\text{U}_3\text{Si}_2\text{-P1}$ structure. We performed GGA+ U +SO calculations to find the U_{eff} at which $\text{U}_3\text{Si}_2\text{-P4}/mbm$ has lower enthalpy than the $\text{U}_3\text{Si}_2\text{-P1}$ structure. The U_{eff} value for this is approximately 1.3 eV and the magnetic moment increased to $1.9 \mu_B$ per uranium atom for $\text{U}_3\text{Si}_2\text{-P4}/mbm$.

At $U_{\text{eff}} = 1.3$ eV, the different U_3Si_2 and USi structures are energetically similar and it is not clear whether GGA+SO or GGA+ U +SO is appropriate. Thus, we determined the convex hull at $U_{\text{eff}} = 1.5$ eV as shown in Figure 2 (structural properties are given in Table 2). Increasing U_{eff} has a profound effect on the enthalpy for ferromagnetic compounds (USi_2 , USi-Pnma and $\text{U}_3\text{Si}_2\text{-P4}/mbm$), but non-magnetic compounds (USi_3 , USi-Imma , $\text{U}_3\text{Si}_2\text{-P1}$, U_2Si and U_3Si) do not see such a large change. Note that using GGA+ U +SO at $U_{\text{eff}} = 1.5$ eV would negate the stability of the presented experimentally inconspicuous USi-Imma and U_2Si structures, as these would not be on the convex hull. Thus, the convex hulls for GGA and GGA+ U calculations are fundamentally different and must be carefully taken into account when assessing the thermodynamic behavior of the U-Si

system. It is not uncommon for different U_{eff} values to be used for different phases (e.g. uranium-oxygen system), which would recover the current interpretation of the experimental phase diagram for the U-Si system. We point out that there have been methods developed that investigate compound formation enthalpy using a combination of GGA and GGA+ U methods [64,65]. The motivation for such an approach is that the unary uranium metal system as well as metal-rich compounds are often not well described by high U values and the preferred choice is typically to use GGA without any Hubbard U parameter ($U_{\text{eff}} = 0.0$ eV).

Figure 1. The convex hull for U-Si compounds using GGA and GGA+SO. The blue diamonds and red triangles represent GGA calculations from VASP and WIEN2k, respectively. The solid black circles are GGA+SO calculations from WIEN2k, which has the convex hull marked by a dashed line. The green boxes are guides for the eye that highlight USi - $Pnma$ and U_3Si_2 - $P4/mbm$ values.

Figure 2. The convex hull for U-Si compounds using GGA+SO and GGA+*U*+SO calculations (both in WIEN2k). Black circles and corresponding dashed lines are the same GGA+SO values given in Figure 1. Blue diamonds and corresponding dashed blue line are GGA+*U*+SO calculations with $U_{\text{eff}} = 1.5$ eV. The green boxes are guides for the eye that highlight USi-*Pnma* and U_3Si_2 -*P4/mbm* values. Red triangles and corresponding dashed line represents the convex hull from CALPHAD [66].

Table 1. Structural properties of the U-Si compounds calculated in this work using GGA.

Compound	Space group	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Z	Wyckoff Positions
U_2Si	#15, <i>C2/c</i>	8.483	5.299	6.562	90	127.8	90	4	U: 8f (0.334, 0.138, 0.717) Si: 4e (0, 0.859, $\frac{1}{4}$)
U_3Si_2	#127, <i>P4/mbm</i>	7.230	7.230	3.891	90	90	90	2	U1: 2a (0, 0, 0) U2: 4h (0.685, 0.185, $\frac{1}{2}$) Si1: 4g (0.885, 0.385, 0)
U_3Si_2	#2, <i>P1</i>	5.272	5.296	7.760	82.1	70.2	66.1	2	U1: 2i (0.107, 0.757, 0.190) U2: 2i (0.703, 0.243, 0.190) U3: 2i (0.316, 0.000, 0.368) Si1: 2i (0.297, 0.229, 0.000) Si2: 2i (0.760, 0.500, 0.479)
USi	#74, <i>Imma</i>	3.967	3.999	9.118	90	90	90	4	U: 4e (0, $\frac{1}{4}$, 0.158) Si: 4e (0, $\frac{1}{4}$, 0.591)
USi	#62, <i>Pnma</i>	8.622	3.590	5.031	90	90	90	4	U: 4c (0.286, $\frac{1}{4}$, 0.866) Si: 4c (0.479, $\frac{1}{4}$, 0.341)

Table 2. Structural properties of the U-Si compounds calculated in this work using GGA+ U with $U_{\text{eff}} = 1.5$ eV.

Compound	Space group	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Z	Wyckoff Positions
U ₂ Si	#15, <i>C2/c</i>	8.513	5.338	6.575	90	127.6	90	4	U: 8f (0.334, 0.136, 0.720) Si: 4e (0, 0.860, ¼)
U ₃ Si ₂	#127, <i>P4/mbm</i>	7.479	7.479	3.975	90	90	90	2	U1: 2a (0, 0, 0) U2: 4h (0.685, 0.185, ½) Si1: 4g (0.885, 0.386, 0)
U ₃ Si ₂	#2, P1	5.291	5.340	7.810	82.1	70.2	65.9	2	U1: 2i (0.112, 0.744, 0.188) U2: 2i (0.700, 0.257, 0.188) U3: 2i (0.314, 0.000, 0.373) Si1: 2i (0.701, 0.778, 0.000) Si2: 2i (0.760, 0.500, 0.479)
USi	#74, <i>Imma</i>	4.029	3.986	9.123	90	90	90	4	U: 4e (0, ¼, 0.844) Si: 4e (0, ¼, 0.410)
USi	#62, <i>Pnma</i>	7.980	3.819	5.676	90	90	90	4	U: 4c (0.317, ¼, 0.385) Si: 4c (0.463, ¼, 0.871)

Figure 3 shows the atomic volume trends for the U-Si system from experiment, GGA and GGA+ U calculations. The experimentally observed USi-*Pnma* and U₃Si₂-*P4/mbm* compounds show much larger volumes as compared to other U-Si compounds. The GGA calculations underestimate the atomic volume for each structure, while GGA+ U slightly overestimates it. In addition, the difference between GGA and GGA+ U volumes tend to be much larger for USi-*Pnma* and U₃Si₂-*P4/mbm* than other structures. This illustrates that the Hubbard U parameter has a larger effect on these ferromagnetic structures. In contrast, the structures found using structural searches with GGA tend to have much smaller volumes. The USi-*Imma*, U₃Si₂-P1 and U₂Si structures show a fairly linear increase in atomic volume with increasing metal concentration.

Figure 3. The atomic volume trends for the U-Si system. The black squares represent experimentally reported structures for U-Si [21,26]. Red triangles and blue diamonds represent GGA and GGA+ U ($U_{\text{eff}} = 1.5$ eV) calculations, respectively. The green boxes are guides for the eye that highlight USi-*Pnma* and U_3Si_2 -*P4/mbm* values.

The predicted ferromagnetic ground-state for U_3Si_2 -*P4/mbm* from DFT differs from experiment, which shows paramagnetism [21,68]. Wang *et al.* [28] have reported structural properties of U_3Si_2 -*P4/mbm* using the same GGA+ U methodology, but there is no mention of the values for magnetic moments. The atomic volumes in Wang *et al.* are smaller than our calculations, but we may reproduce their results when we perform non-magnetic calculations. The enthalpy of formation for a ferromagnetic calculation is -0.016 eV/atom lower than the non-magnetic case (GGA calculations). This represents a significant difference and is also important when increasing U_{eff} . As an example, our GGA+ U +SO calculations show that the formation enthalpy for ferromagnetic U_3Si_2 -*P4/mbm* decreases to -0.55 eV/atom, -0.81 eV/atom and -1.14 eV/atom for $U_{\text{eff}} = 2$ eV, 3 eV and 4 eV, respectively. For reference, the CALPHAD value is -0.36 eV/atom [66]. This signifies that the use of large U_{eff} values should be done with caution. Unfortunately, the inability of GGA and GGA+ U calculations to predict the correct magnetic state for U_3Si_2 -*P4/mbm* is an open issue and is left for future work.

3.2 Electronic Structure

In order to gain further insight into the bonding of these systems, we calculated the total density of states (DOS) and projected density of states (PDOS). Figures 4 and 5 show the DOS and PDOS for USi-*Imma* and U_2Si , respectively. These compounds exhibit metallic bonding. The PDOS for each compound shows that the f-orbital is the major

contributor to bonding around the Fermi energy.

Figure 4. a) The total DOS and b) PDOS for USi-*Imma* using GGA+SO from WIEN2k. The Fermi energy is at 0 eV.

Figure 5. a) The total DOS and b) PDOS for U_2Si using GGA+SO from WIEN2k. The Fermi energy is at 0 eV.

The total DOS for $\text{U}_3\text{Si}_2\text{-P1}$ and $\text{U}_3\text{Si}_2\text{-P4}/mbm$ using GGA+SO is shown in Figure 6. Each of these structures has an enthalpy above the convex hull. The DOS at the Fermi level shows a maximum for each structure, which indicates instability. One major difference between the structures is the width of the DOS for deep energy states. For $\text{U}_3\text{Si}_2\text{-P1}$ (Figure 6a), states are observed between -14 to -19 eV, while the states for $\text{U}_3\text{Si}_2\text{-P4}/mbm$ are much more narrow at around -15 to -18 eV (Figure 6b). These differences are attributed mainly to the uranium p-orbitals (PDOS not shown).

Figure 6. The total DOS for a) $\text{U}_3\text{Si}_2\text{-P1}$ and b) $\text{U}_3\text{Si}_2\text{-P4}/mbm$ using GGA+SO in WIEN2k. The Fermi energy is at 0 eV.

The total DOS and PDOS for the experimentally observed $\text{U}_3\text{Si}_2\text{-P4}/mbm$ at $U_{\text{eff}} = 1.5$ eV is shown in Figure 7. A minimum in the DOS is formed at the Fermi level, signifying the increased stability of the structure with increasing U_{eff} . This is facilitated by the ferromagnetic character of the structure. Our calculated DOS differs from that of Wang *et al.* [28], where a local maximum in the DOS is shown at the Fermi energy. Finally, the DOS for $\text{U}_3\text{Si}_2\text{-P4}/mbm$ using GGA+ U in VASP (not shown) is very similar to the results provided here using WIEN2k. Thus, based on the DOS and enthalpy calculations, we conclude that semi-core electrons do not play a significant role in bonding.

a)

Figure 7. The a) total DOS and b) PDOS for $\text{U}_3\text{Si}_2\text{-P4/mbm}$ using GGA+U+SO at $U_{\text{eff}} = 1.5$ eV in WIEN2k. Positive values are spin-up electrons, while negative values are spin-down electrons. The Fermi energy is at 0 eV.

3.3 Mechanical and Dynamical Properties

The phonon dispersion curves for select U-Si compounds using GGA without model corrections are shown in Figure 8. No imaginary phonon frequencies are observed for USi-Imma and U_2Si , which signifies dynamic stability. However, $\text{U}_3\text{Si}_2\text{-P1}$ and $\text{U}_3\text{Si}_2\text{-P4/mbm}$ show imaginary frequencies, meaning that they are dynamically unstable. The elastic properties for stable USi-Imma and U_2Si are reported in Table 3. Additional calculations for $\alpha\text{-USi}_2$, $\beta\text{-USi}_2$ and USi_3 phases are shown in Table 4 and compared to a previous DFT study [27]. In contrast to that work [27], we find $\beta\text{-USi}_2$ to be mechanically stable based on the Born stability criteria [69]. As the values for $\alpha\text{-USi}_2$ and USi_3 are similar between their work and ours (Table 4), it is not known why $\beta\text{-USi}_2$ would be significantly different. We posit that the differences between their approach (CASTEP software and the volume-conserving method) and ours should not lead to qualitatively

different results and speculate that the discrepancy is an energy convergence issue.

Figure 9 shows the phonon dispersion curves for $\text{U}_3\text{Si}_2\text{-}P4/mbm$ and $\text{USi-}Pnma$ using GGA+ U with $U_{\text{eff}} = 1.5$ eV. For $\text{USi-}Pnma$, the instability (Figure 9b) is not surprising since this structure is believed to be stabilized by oxygen [26]. For $\text{U}_3\text{Si}_2\text{-}P4/mbm$, a very small imaginary frequency is observed at the Γ -point. The instability is further reduced for additional calculations at $U_{\text{eff}} = 2.5$ eV (not shown). We have not been able to identify any new structure resulting from the instability, which could instead be a sign of a small local distortion driven by symmetry breaking (potentially a superstructure highly related to the $P4/mbm$ structure). The elastic constants for $\text{U}_3\text{Si}_2\text{-}P4/mbm$ are shown in Table 5 and prove to be mechanically stable [69]. The values of the elastic properties from this work differ from Wang *et al.* [28], but this is due to the different U_{eff} values used and magnetism considerations. Unfortunately, no experimental results on elastic properties for $\text{U}_3\text{Si}_2\text{-}P4/mbm$ are reported. The ratio of bulk to shear moduli (B/G) may be used as a metric to qualitatively describe bonding behavior. A $B/G > 1.75$ suggests that a material is ductile, while values less than 1.75 implies a material is brittle [70]. All of the U-Si compounds considered in this work are brittle, agreeing with experimental observations [71].

Figure 8. The phonon dispersion curves for a) U_2Si , b) $USi-Imma$, c) U_3Si_2-P1 and d)

U_3Si_2 -*P4/mbm* using GGA.

Table 3. The calculated elastic constants for predicted U-Si compounds from this work for GGA calculations. Units for B, G and C_{ij} are GPa.

	Space Group	B	G	C_{11}	C_{22}	C_{33}	C_{44}	C_{66}	C_{13}	C_{23}	C_{15}	C_{25}	C_{35}	C_{46}
U_2Si	#15, <i>C2/c</i>	128	82	290	235	292	77	49	74	77	-12	2	2 0	1
USi	#74, <i>Imma</i>	147	91	283	215	239	24	113	69	82	--	--	--	--

Table 4. The calculated elastic constants for various U-Si compounds from this work and Ref. [27] for GGA calculations. Units for B, G and C_{ij} are GPa.

	B	G	B/G	C_{11}	C_{33}	C_{44}	C_{66}	C_{12}	C_{13}
α - USi_2 (ThSi ₂ -type; This work)	102	71	1.43	166	161	69	125	96	60
α - USi_2 Ref. [27]	116	70	1.66	189.8	179.0	77.7	106.5	103.5	71.3
β - USi_2 (AlB ₂ -type; This work)	126	72	1.74	197	182	116	--	132	74
β - USi_2 Ref. [27]	115	101	1.13	10.1	200.4	80.1	--	292.0	58.2
USi_3 (This work)	134	103	1.30	240	--	118	--	80	--
USi_3 Ref. [27]	125.93	92.13	1.37	230.9	--	102.3	--	73.4	--

Figure 9. The phonon dispersion curves for a) $\text{U}_3\text{Si}_2\text{-P4}/mbm$ and b) USi-Pnma using GGA+ U at $U_{\text{eff}} = 1.5$ eV.

Table 5. The calculated elastic constants for $\text{U}_3\text{Si}_2\text{-P4}/mbm$ using GGA+ U at $U_{\text{eff}} = 1.5$ eV (this work). Units for B, G and C_{ij} are GPa.

	Space Group	B	G	B/G	C_{11}	C_{33}	C_{44}	C_{66}	C_{12}	C_{13}
U_3Si_2	#127, $P4/mbm$	81	53	1.53	149	139	63	46	49	48

4. Conclusions

We have performed GGA and GGA+ U calculations for the U-Si system with the inclusion of spin-orbit coupling. The convex hull is calculated at various U_{eff} values in order to survey the effect of Hubbard U on the relative energetics and structural properties of the various phases. Structure prediction calculations were performed to search for alternative structures at select compositions. Three new structure-types are posited (USi-Imma , $\text{U}_3\text{Si}_2\text{-P1}$, U_2Si), which contribute to the construction of the simulated convex hull for GGA calculations ($U_{\text{eff}} = 0$ eV).

It is seen that the energetics of $\text{U}_3\text{Si}_2\text{-P4}/mbm$ is greatly affected by the DFT description used. For GGA and GGA+SO calculations, the experimentally observed $\text{U}_3\text{Si}_2\text{-P4}/mbm$ is not predicted to be stable on the convex hull. The theoretical $\text{U}_3\text{Si}_2\text{-P1}$ structure has

much lower enthalpy than the $\text{U}_3\text{Si}_2\text{-}P4/mbm$ for these calculations, but this still lies above the convex hull. The relative stability of $\text{U}_3\text{Si}_2\text{-}P1$ versus $\text{U}_3\text{Si}_2\text{-}P4/mbm$ is reversed for GGA+ U +SO calculations with a U_{eff} approximately >1.3 eV. The phonon dispersion curves for $\text{U}_3\text{Si}_2\text{-}P4/mbm$ at $U_{\text{eff}} = 1.5$ eV show a small instability, which may be reduced by further increasing U_{eff} or imply a small distortion or superstructure in the U_3Si_2 related to $P4/mbm$. Finally, we note that the ferromagnetic behavior of $\text{U}_3\text{Si}_2\text{-}P4/mbm$ is in contradiction to current experimental results. Other computational methodologies may be needed to resolve the discrepancy. These results point towards the need for additional computational and experimental work to better understand the complicated bonding behavior seen in this and many other uranium-based binary systems.

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