Structure Determination and Stability for Pa-Si, Np-Si and U-X-Si (X = Mo, Th, Np) Phases from First-Principles

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Abstract

Density functional theory (DFT) calculations are performed for Pa-Si, Np-Si and uranium-based ternary silicide phases. Structure prediction calculations are used to search for competing phases in these systems. Results using the generalized gradient approximation (GGA), on-site Coulomb correction (GGA+*U*) and van der Waals interactions are presented. All Pa-Si compounds reported here are structurally analogous to those found in other actinide silicide systems. The electronic structure of Pa₃Si₂ shows the f-orbital electrons are largely unoccupied, which is in contrast to calculations for Np₃Si₂. For the Np-Si system, predicted stable structures using GGA differ from the experimentally observed structures, which, however, are energetically preferred in results using the GGA+*U* method. Structure searches for U₂MoSi, U₂ThSi₂ and UNpSi reveal dynamically stable ternary compounds. The phonon dispersion curves, elastic constants and electronic density of states for the various phases are compared to those from previous DFT calculations for U-Si phases.

1. Introduction

Uranium silicide compounds are gaining interest for use in nuclear fuels, both as a second phase in composite systems and as a stand-alone fuel [1,2]. For composite systems, various U-Si phases are being explored for use, for example, as protective layers on UN particles in fuel [3,4]. The U₃Si₂ phase, in particular, is an attractive candidate to add to UN fuels because it offers improved resistance to reaction with water while also providing for high uranium loading and good thermal conductivity. Before fuels containing U-Si compounds can be licensed for use in light water reactors, a better understanding of material properties is critically needed in areas such as thermal conductivity, fission product behavior and reactions with air and steam.

The burnup process will naturally result in the production of the transmutation products Pa and Np. These may form silicides in the fuel, and their stability and behavior are therefore important to understand. In addition, since Pa and Np are radioactive and have long half-lives, an understanding of their thermodynamic behavior with Si is crucial for waste disposition. Studying relationships among all the actinide silicide systems also allows trends in bonding to be observed, which aids in the fundamental understanding of U-Si compounds [5-8]. However, the rarity of Pa/Np and the requirement of specialized laboratories to perform experimental work has resulted in no reports on Pa-Si and only a few studies on Np-Si [9-11]. The few studies on Np-Si compounds suggest their structural properties are similar to those in the Th-Si and U-Si systems [12,13].

We use density functional theory (DFT) to explore the energetics, structural stability and electronic structure of various actinide silicide compounds. Previous work by the authors using DFT showed notable discrepancies between the GGA and GGA+*U* methods in the U-Si system [5]. Thus, we explore the effect of various DFT methods on material properties where it is deemed appropriate. Since only a few studies have been performed for these systems, we use a structure prediction algorithm to search for additional energetically competing phases. For the Np-Si system, structure searches using GGA and the inclusion of van der Waals forces reveal dynamically stable structures that differ crystallographically from the known experimental structures. We show how the use of GGA+*U* changes the experimental phases to be energetically preferential, which was also required for U-Si phases [5].

In addition to Pa-Si and Np-Si phases, we explore whether uranium-based ternary silicide compounds may also be predicted using DFT. These attempts are aimed at accelerating materials discovery and provide an understanding of the bonding behavior in these materials. The DFT methods used in this work may aid experimental structure determination, particularly in areas where insufficient annealing conditions may have generated non-equilibrium phases with concentration gradients. This strategy shows promise for select U-Mo-Si, U-Th-Si and U-Np-Si phases, as new structures are predicted in this work. However, a thorough investigation of the thermodynamic properties is required before committing these new phases to their respective phase diagrams.

2. Computational Details

We perform structure predictor calculations in CALYPSO [14,15] using VASP [16-18] for the energy calculation. The projector augmented wave (PAW) potentials with a plane-wave energy cutoff of 325 eV are used for the structure searches. The Perdew-Burke-Ernzerhof (PBE) [19] functional of the generalized gradient approximation (GGA) is used for the exchange-correlation potential. The van der Waals interactions are modeled with the “D3” method of Grimme *et al.* [20]. Fixed composition structure searches using GGA and GGA+D3 are performed for PaSi₂, PaSi, Pa₂Si, Np₃Si, Np₂Si, Np₃Si₂, NpSi and NpSi₂. The maximum unit cell size is set to four formula units for Pa-Si

and Np-Si searches. Structural searches for U_2MoSi , U_2ThSi_2 and $UNpSi$ are performed using GGA only and allowing up to two formula units.

The symmetry of the final structures is determined by a tolerance factor in CALYPSO, which was varied in order to obtain alternative symmetry settings. The new structures tend to have low symmetry as evidenced by their symmetry being in the monoclinic and triclinic crystal systems, but that may be an artifact of the methods used. A different symmetry setting and DFT method might lower the enthalpy slightly, which was observed in similar studies for U_2Mo [22,23]. Space groups and Wyckoff positions are determined using FINDSYM [21]. A nomenclature of combined a formula unit and space group is used for the Np-Si system where multiple unique structures may be present.

The enthalpy of formation is calculated as:

$$\Delta H = \frac{E_{MSi}^{total} - \sum n_X E_X^{atom}}{\sum n_X} \quad \text{Eq. 1}$$

Here, E_{MSi}^{total} is the total energy of the actinide silicide compound, E_X^{atom} is the energy per atom in the appropriate reference state ($X = \alpha\text{-Pa}$, $\alpha\text{-Np}$ or diamond-Si) and n_X is the number of atoms for each species in the compound. For all reported calculations, the plane-wave cutoff is increased to 500 eV. A Monkhorst-Pack (MP) mesh [24] is used to sample the Brillouin zone. AFLOW online [25,26] is used to determine the k -point mesh for a given structure. Here, meshes of approximately 5,000 k -points per reciprocal atom are used, which results in converged enthalpy values. Spin-orbit coupling (SOC) is not included in the calculations, which will slightly alter the formation enthalpy at zero Kelvin. For practical applications, such as the generation of phase diagrams, finite temperature thermophysical properties will need to be calculated. This will require more advanced methods (e.g., quasiharmonic approximation or *ab initio* molecular dynamics) and is outside the scope of this work.

The enthalpies of Np-Si phases are analyzed using GGA, the on-site Coulomb correction (GGA+ U) method and van der Waals interactions. The GGA+ U method is widely used to explore the correlated nature of $5f$ electrons. For the current implementation [27], only an effective value, U_{eff} , is used (the exchange parameter, J , is set to zero). We treat U_{eff} as a variable parameter in order to explore the significant enthalpy differences observed between experimental structures and those found from the structure predictor calculations. While the use of GGA+ U may lead to metastable electronic structure solutions, we find the effect to be minimal. For example, spot checks for different Np-Si phases using GGA+ U ($U_{\text{eff}} = 1.0$ eV) results in an enthalpy difference of about 0.01 eV/atom as compared to using the U -ramping method [28].

The phonon dispersion curves are calculated with the PHONOPY software [29]. Here, GGA calculations used the finite displacement method [30], while GGA+ U calculations used the density functional perturbation theory (DFPT) method [31]. This is in line with our previous calculations for U-Si phases [5], where DFPT showed better convergence for ferromagnetic phases. Phonon calculations for GGA+D3 using the finite

displacement method were performed for many of the predicted structures. The GGA+D3 results showed only small differences in the phonon frequencies as compared to GGA results, so only GGA results are shown for brevity. Also to note, phonon calculations for the D3 method using DFPT cannot be performed because the contribution to the interatomic force constants is currently not implemented in VASP, although Van Troeye *et al.* [32] have recently implemented DFT-D in the ABINIT software. All phonon calculations use $2 \times 2 \times 2$ supercells. AFLOW online is used to determine high symmetry pathways [25,26]. The *k*-meshes for the phonon calculations are provided in the Appendix. The elastic constants are calculated using a stress-strain method in VASP [33].

The various DFT methods used in this work (GGA, GGA+D3, GGA+*U*, GGA+D3+*U*) provide only an initial examination of the complicated bonding behavior of these actinide silicides. There are no experimental data for the Pa-Si system and the ternary compounds to use in comparison, so only GGA calculations are performed. There are some data for the Np-Si system exhibiting extensive disagreement with our GGA calculations. In such a situation, one may have to “climb” Jacob’s Ladder [34], where increasingly complex (and computationally expensive) exchange-correlation functionals may be required to resolve the discrepancies [35]. Future work on these systems may need to use alternative GGA+*U* implementations [36,37] or hybrid functionals [38,39].

3. Results and Discussion

3.1 Np-Si System

There are six Np-Si structures observed in experimental efforts [9-11]. These include two NpSi_{2-x} structures (AlB₂-type and ThSi₂-type), NpSi₃-*Pm* $\bar{3}$ *m* (AuCu₃-type), NpSi-*Pnma* (FeB-type), NpSi-*Cmcm* (own type) and Np₃Si₂-*P4/mbm* (U₃Si₂-prototype). Interestingly, the NpSi-*Pnma* structure is reported for sample compositions ranging from 44-60 at.% Si, while NpSi-*Cmcm* is observed only for an equiatomic composition [9]. A full exploration of the effects of point defects on structural stability is outside the scope of this work. The highest Np concentration experimentally studied was 60 at.% Np, so additional Np-rich phases cannot be ruled out. In the current effort, we explore the phase stabilities using the noted DFT methodologies.

3.1.1 Np-Si convex hull

Structural searches using GGA and GGA+D3 reveal five unreported structures: Np₂Si-*P* $\bar{1}$, Np₃Si₂-*C2/m*, NpSi-*C2/m*, NpSi₂-*C2/m* and NpSi₂-*P2/m*. These new structures are crystallographically unique as compared to other known actinide silicide compounds, including the U-Si structures found in a previous DFT work [5]. (See the Appendix for their structural details.) The Np₂Si-*P* $\bar{1}$ structure was found using GGA calculations. Searches for phases with higher Si concentrations (> 33at.% Si) using GGA calculations tended to give structures of lower stability. Instead, the Np₃Si₂-*C2/m*, NpSi-*C2/m*, NpSi₂-*C2/m* and NpSi₂-*P2/m* structures were found using GGA+D3.

Figure 1 shows the Np-Si convex hull from GGA and GGA+D3 calculations. For GGA calculations (Figure 1a), there are three compounds on the convex hull: $\text{NpSi}_3\text{-Pm}\bar{3}m$, NpSi-C2/m and $\text{Np}_2\text{Si-P}\bar{1}$. $\text{Np}_3\text{Si}_2\text{-C2/m}$ is 18 meV/atom above the convex hull formed by NpSi-C2/m and $\text{Np}_2\text{Si-P}\bar{1}$. All four of the NpSi_2 structures are above the hull by 7, 12, 15 and 20 meV/atom for $\text{NpSi}_2\text{-P6/mmm}$, $\text{NpSi}_2\text{-P2/m}$, $\text{NpSi}_2\text{-I4}_1\text{/amd}$ and $\text{NpSi}_2\text{-C2/m}$, respectively. The three experimental structures with the highest Np concentration are all very far from the convex hull. For the NpSi phase, the enthalpy for NpSi-Cmcm is 29 meV/atom lower than NpSi-Pnma , but NpSi-Cmcm is still 152 meV/atom above the convex hull formed by NpSi-C2/m . One noted difference between GGA calculations and experiment is the magnetic behavior of $\text{NpSi}_3\text{-Pm}\bar{3}m$. The calculated magnetic moment per Np atom for $\text{NpSi}_3\text{-Pm}\bar{3}m$ is $1.9 \mu_B$. In contrast, Mössbauer absorption experiments show non-magnetic behavior [11].

For GGA+D3 calculations (Figure 1b), there are four compounds on the convex hull: $\text{NpSi}_3\text{-Pm}\bar{3}m$, $\text{NpSi}_2\text{-C2/m}$, NpSi-C2/m and $\text{Np}_2\text{Si-P}\bar{1}$. The $\text{NpSi}_2\text{-P2/m}$, $\text{NpSi}_2\text{-P6/mmm}$ and $\text{NpSi}_2\text{-I4}_1\text{/amd}$ structures are 21, 71 and 94 meV/atom higher in enthalpy than $\text{NpSi}_2\text{-C2/m}$. As seen in the GGA calculations, $\text{Np}_3\text{Si}_2\text{-C2/m}$ is above the convex hull by 14 meV/atom. Also, the two NpSi experimental structures are far from the hull and $\text{Np}_3\text{Si}_2\text{-P4/mbm}$ is even predicted to have a positive enthalpy of formation. The enthalpy for NpSi-Cmcm is 25 meV/atom lower than that for NpSi-Pnma .

Figure 1. The convex hull for Np-Si compounds using a) GGA and b) GGA+D3.

Next, we apply the GGA+ U formalism to explore its effect on the formation enthalpy, since the experimental structures are computed to have high enthalpy values in GGA and GGA+D3 calculations. This approach was needed to make experimental structures energetically favorable for the U-Si system as well [5]. We incrementally increased U_{eff} by 0.1 eV to search for the value at which the experimental $\text{Np}_3\text{Si}_2\text{-P4}/mbm$ structure has a lower enthalpy than predicted $\text{Np}_3\text{Si}_2\text{-C2}/m$. This transition occurs at approximately $U_{\text{eff}} = 0.8$ eV for GGA+ U and at $U_{\text{eff}} = 1.2$ eV for GGA+D3+ U . To avoid ambiguity in the competing structures at the transition point, we show the convex hull for GGA+ U with $U_{\text{eff}} = 1.0$ eV and GGA+D3+ U with $U_{\text{eff}} = 1.5$ eV (Figure 2). The U_{eff} values for the Np-Si system in this work are similar to those for U-Si [5], U-Zr [40,41] and Np-Zr [42].

For GGA+ U calculations with $U_{\text{eff}} = 1.0$ eV (Figure 2a), there are three structures on the convex hull: $\text{NpSi}_2\text{-P6}/mmm$, NpSi-Cmcm and $\text{Np}_3\text{Si}_2\text{-P4}/mbm$. The enthalpy for NpSi-Cmcm is 10.4 meV/atom lower than that of NpSi-Pnma . The $\text{NpSi}_3\text{-Pm}\bar{3}m$ structure is 52.9 meV/atom above the convex hull, which demonstrates that GGA+ U should be used with caution for the different phases. This is due to the decrease in enthalpy for $\text{NpSi}_2\text{-P6}/mmm$, whose value is -0.264 eV/atom for GGA and -0.521 eV/atom for GGA+ U . The structures found using GGA and GGA+D3 ($\text{Np}_2\text{Si-P}\bar{1}$, $\text{Np}_3\text{Si}_2\text{-C2}/m$, $\text{NpSi-C2}/m$, $\text{NpSi}_2\text{-C2}/m$ and $\text{NpSi}_2\text{-P2}/m$) all have enthalpy values that are far above the convex hull. Figure 2b shows the convex hull for GGA+D3+ U , which indicates similar behavior to that for GGA+ U calculations. The enthalpy for NpSi-Cmcm is 56 meV/atom lower than that for NpSi-Pnma for GGA+D3+ U , which implies that this method is not expected to be as accurate as GGA+ U if these two structures are supposed to be nearly degenerate in enthalpy.

The magnetic behavior is very different than that determined for reported experimental structures and those predicted by DFT. The predicted structures ($\text{Np}_2\text{Si-P}\bar{1}$, $\text{Np}_3\text{Si}_2\text{-C2}/m$, $\text{NpSi-C2}/m$, $\text{NpSi}_2\text{-C2}/m$ and $\text{NpSi}_2\text{-P2}/m$) are all non-magnetic. In contrast, the

magnetic moment per Np atom for $\text{NpSi-}Pnma$, $\text{NpSi-}Cmcm$, and $\text{Np}_3\text{Si}_2\text{-}P4/mbm$ are $4.6 \mu_B$, $4.3 \mu_B$ and $4.2 \mu_B$, respectively (using GGA+ U at $U_{\text{eff}} = 1.0 \text{ eV}$). Mössbauer absorption experiments and X-ray photoemission spectroscopy are needed towards the Np-rich portion of the phase diagram to aid in understanding the electronic structure. As noted elsewhere [43], GGA+ U should be used with caution as it may lead to spurious magnetic properties.

Figure 2. The convex hull for Np-Si compounds using a) GGA+ U with $U_{\text{eff}} = 1.0 \text{ eV}$ and b) GGA+D3+ U with $U_{\text{eff}} = 1.5 \text{ eV}$.

3.1.2 Np-Si dynamical and elastic properties

Figures 3 and 4 shows phonon dispersion curves for Np-Si structures using GGA. No imaginary frequencies are observed in the phonon spectra, which signifies dynamic stability. This is important because thermodynamic properties may be extracted from these calculations, which may then be used as inputs for thermodynamic models. Figure 5 shows the phonon dispersion curves for Np_3Si_2 - $P4/mbm$ using GGA and GGA+ U . As was the case for our previous work on U_3Si_2 [5], Np_3Si_2 - $P4/mbm$ is dynamically unstable.

Tables 1 and 2 show the elastic constants for various structures using GGA and GGA+ U , respectively. As shown in Table 1, the new Np-Si structures have negative values for some of the off-diagonal elastic constants. A discussion on elastic stability and the sufficient and necessary criteria for different crystal systems is given in Ref. [44]. Closed form expressions for the elastic stability of monoclinic and triclinic crystal systems was not presented in that work. However, we calculated the eigenvalues of the elastic matrix and all the values are positive. Thus, the new structures are all elastically stable according to the Born criteria.

Figure 3. The phonon dispersion curves for a) $\text{Np}_2\text{Si}-P\bar{1}$ b) $\text{Np}_3\text{Si}_2-C2/m$, c) $\text{NpSi}-C2/m$ and d) $\text{NpSi}_3-Pm\bar{3}m$ using GGA.

Figure 4. The phonon dispersion curves for NpSi₂ structures using GGA. a) NpSi₂-P6/mmm, b) NpSi₂-I4₁/amd, c) NpSi₂-C2/m and d) NpSi₂-P2/m.

Figure 5. The phonon dispersion curves for Np₃Si₂-P4/mbm using a) GGA and b) GGA+U with $U_{eff} = 1.0$ eV.

Table 1. The calculated elastic properties for Np-Si compounds using GGA.

	Np ₂ Si #2, $P\bar{1}$	Np ₃ Si ₂ #12, C2/m	NpSi #12, C2/m	NpSi ₂ #191, P6/mmm	NpSi ₂ #141, I4 ₁ /amd	NpSi ₂ #12, C2/m	NpSi ₂ #10, P2/m	NpSi ₃ #221, Pm $\bar{3}$ m
B (GPa)	161	139	126	109	115	141	128	96
G (GPa)	98	99	83	63	56	106	91	85
B/G	1.65	1.40	1.52	1.74	2.04	1.33	1.40	1.14
C _{ij} (GPa)								
C ₁₁	261	176	165	186	131	229	214	171
C ₂₂	330	336	325			326	213	
C ₃₃	379	268	181	126	168	294	287	
C ₄₄	100	123	115	95	63	150	75	103
C ₅₅	49	92	69			70	91	
C ₆₆	116	114	104		99	105	131	
C ₁₂	124	110	36	106	106	88	103	58
C ₁₃	94	80	110	71	79	72	54	
C ₁₄	-9							
C ₁₅	-29	-8	9			-19	-17	
C ₁₆	-9							
C ₂₃	76	90	143			74	81	
C ₂₄	-17							

C ₂₅	3	-3	-43			15	8	
C ₂₆	19							
C ₃₄	29							
C ₃₅	9	20	4			-2	-27	
C ₃₆	-8							
C ₄₅	-19							
C ₄₆	-15	-18	14			14	-2	
C ₅₆	3							

Table 2. The calculated elastic properties for Np-Si compounds using GGA+ U with $U_{eff} = 1.0$ eV.

	Np ₃ Si ₂ #127, $P4/mbm$	NpSi #62, $Pnma$	NpSi #63, $Cmcm$
B (GPa)	77	78	75
G (GPa)	41	49	52
B/G	1.86	1.60	1.45
C _{ij} (GPa)			
C ₁₁	125	127	137
C ₂₂		138	106
C ₃₃	118	137	154
C ₄₄	51	43	64
C ₅₅		32	84
C ₆₆	36	85	23
C ₁₂	61	45	37
C ₁₃	31	59	57
C ₂₃		46	43

3.1.3 Np-Si electronic structure

The electronic density of states (DOS) and projected density of states (PDOS) for various structures are calculated to gain insight into the bonding of the different structures. The DOS for Np₃Si₂- $C2/m$, Np₂Si- $P\bar{1}$ and NpSi- $C2/m$ from GGA calculations are shown in Figures 6 and 7. They each display similar features, with a large occupancy around the Fermi level. The PDOS for Np₃Si₂- $C2/m$ (Figure 6b) shows the Np f-orbitals are the dominant contribution at the Fermi level and no distinct maxima or minima is observed. This qualitatively matches the electronic structure for USi- $Imma$ and U₂Si structures found in our previous work [5].

The DOS for the experimental Np-Si structures from GGA+ U calculations are shown in Figures 8 and 9. The three structures show similar features, most noticeably in the fewer occupied states at the Fermi level as compared to the predicted structures. The PDOS for Np₃Si₂- $P4/mbm$ (Figure 8b) shows a distinct minimum in the Np f-orbitals at the Fermi level, in qualitative agreement with the uranium f-orbital behavior for U₃Si₂ seen in previous calculations [5].

Figure 6. The a) total DOS and b) PDOS $\text{Np}_3\text{Si}_2\text{-C2/m}$. The calculations used GGA. The Fermi energy is set to 0 eV.

Figure 7. The total DOS for a) $\text{Np}_2\text{Si-P}\bar{1}$ and b) $\text{NpSi-C2}/m$. The calculations used GGA. The Fermi energy is set to 0 eV.

Figure 8. The a) total DOS and b) PDOS for $\text{Np}_3\text{Si}_2\text{-P4}/mbm$. The calculations used GGA+ U at $U_{\text{eff}} = 1.0$ eV. Positive values are spin-up electrons, while negative values are spin-down electrons. The Fermi energy is set to 0 eV.

Figure 9. The total DOS for a) NpSi-*Pnma* and b) NpSi-*Cmcm*. The calculations used GGA+*U* at $U_{\text{eff}} = 1.0$ eV. Positive values are spin-up electrons, while negative values are spin-down electrons. The Fermi energy is set to 0 eV.

3.2 Pa-Si System

Structural searches for Pa-Si compounds using GGA+D3 did not reveal any structures different from those found using GGA. The GGA+*U* method was not used because there are no obvious discrepancies with other actinide silicide systems and there are no Pa-Si experimental results to compare with. Other DFT studies show that GGA adequately describes Pa metal and the Pa-N system [45-47]. Thus, only GGA results are reported here.

3.2.1 Pa-Si convex hull

The convex hull showing the phases with the lowest enthalpy relative to Si and α -Pa [48] are shown in Figure 10. The following compositions are on the convex hull: Pa_3Si , Pa_3Si_2 , PaSi_2 and PaSi_3 . The two structure types for PaSi_2 (AlB₂-type and ThSi₂-type) are close in formation enthalpy, where the enthalpy for the ThSi₂-type is 3 meV/atom lower. The Pa_3Si phase is actually about 10.4 meV/atom above the convex hull, but it is dynamically and elastically stable. All Pa-Si phases are non-magnetic.

Each of the aforementioned Pa-Si phases show analogues in other light-actinide silicide systems (see Appendix for structural details). Pa_3Si and PaSi_3 are AuCu₃-type structures, which are isostructural to polymorphs observed in the U-Si system [49].

Pa_3Si_2 is isostructural to the U_3Si_2 -prototype [13]. The lowest enthalpy structure for PaSi is the FeB-type, which is observed in the Th-Si system [12]. However, PaSi is 30.1 meV/atom above the convex hull. Structural searches for Pa_2Si did not reveal any structures near the convex hull.

Figure 10. The convex hull for Pa-Si compounds using GGA.

3.2.2 Pa-Si dynamical and elastic properties

The dynamic stability for Pa-Si structures are shown in Figure 11. The elastic properties are listed in Table 3 and each are elastically stable as determined by the Born stability criteria [44]. Interestingly, the phonon spectra for Pa_3Si and PaSi_3 show deep minima at the R-point. This indicates that the structures may be easily susceptible to becoming unstable from influences such as pressure or strain.

Figure 11. The phonon dispersion curves for a) Pa_3Si , b) Pa_3Si_2 , c) PaSi_2 (AlB₂-type), d) PaSi_2 (ThSi₂-type) and e) PaSi_3 . The calculations used GGA.

Table 3. The calculated elastic properties for Pa-Si compounds using GGA.

	Space Group	B	G	B/G	C_{11}	C_{33}	C_{44}	C_{66}	C_{12}	C_{13}
Pa_3Si	#221, $Pm\bar{3}m$	112	69	1.63	138		101		98	
Pa_3Si_2	#127, $P4/mbm$	121	66	1.83	197	153	88	57	62	97
PaSi_2	#191, $P6/mmm$	133	60	2.22	184	206	98		141	92
PaSi_2	#141, $I4_1/amd$	132	70	1.89	193	205	71	111	115	93
PaSi_3	#221, $Pm\bar{3}m$	123	84	1.47	222		92		74	

The electronic DOS and PDOS for Pa_3Si_2 using GGA is shown in Figure 12. As for the U-Si and Np-Si phases, Pa_3Si_2 displays metallic bonding due to the partially occupied states at the Fermi level. The main feature that contrasts Pa_3Si_2 with isostructural U_3Si_2 and Np_3Si_2 is that the Pa f-electrons are essentially unoccupied (Figure 12b). This also leads to Pa_3Si_2 being non-magnetic, while isostructural U_3Si_2 and Np_3Si_2 are ferromagnetic in DFT calculations. Thus, the use of GGA+ U is not expected to greatly alter the enthalpy for Pa_3Si_2 , but is critical for U_3Si_2 and Np_3Si_2 stability.

Figure 12. The a) total DOS and b) PDOS for Pa_3Si_2 from GGA calculations. The Fermi energy is set to 0 eV.

3.3 U_2MoSi , U_2ThSi_2 and UNpSi Phases

The multiple metal-rich phases in the actinide-silicide series predicted by GGA calculations raises the question as to whether ternary compounds may also be predicted. These would naturally form as the result of the generation of additional elements through formation of fission or transmutation products, or intentionally as complex alloy fuel compositions. For example, ternary phases have been identified in the U-Mo-Si system [50,51], where a $\text{U}_4\text{Mo}(\text{Mo}_x\text{Si}_{1-x})\text{Si}_2$ phase is a candidate for use as a protective coating for U-Mo fuels [52].

A comprehensive search over composition space is outside the scope of this work, but informed trials examining U_2MoSi , U_2ThSi_2 and UNpSi are performed. The formula U_2MoSi was chosen because a U/Si ratio ranging from 0.6 to 1.6 has been observed

experimentally [53]. In addition, U_2ThSi_2 and $UNpSi$ are analogous to the highest metal concentration for the binary Th-Si and Np-Si systems. Three new possible structures are revealed at these compositions and these are crystallographically unique with respect to the other structures determined in the current effort and in the U-Si system in general (see Appendix for structural details).

3.3.1 U_2MoSi , U_2ThSi_2 and $UNpSi$ dynamical and elastic properties

Figure 13 shows the phonon dispersion curves for U_2MoSi , U_2ThSi_2 and $UNpSi$. Each compound is dynamically stable as no imaginary phonon frequencies are observed. The elastic constants are shown in Table 4 and each structure is also elastically stable. The dynamical stability means that the thermodynamic properties, thermal conductivity and other properties may be readily calculated with DFT. This may be useful in studying how fuel performance may change in localized regions of the fuel, especially at the pellet rim where the highest concentration of fission and transmutation products will be generated.

Figure 13. The phonon dispersion curves for a) U_2MoSi b) U_2ThSi_2 and c) $UNpSi$ using GGA.

Table 4. The calculated elastic properties for U_2MoSi , U_2ThSi_2 and $UNpSi$ phases using GGA.

	U_2MoSi #139, $I4/mmm$	U_2ThSi_2 #12, $C2/m$	$UNpSi$ #11, $P2_1/m$
B (GPa)	168	107	133
G (GPa)	75	70	71
B/G	2.24	1.53	1.87
C_{ij} (GPa)			
C_{11}	220	234	159
C_{22}		190	258
C_{33}	256	216	239
C_{44}	76	24	110
C_{55}		77	71
C_{66}	125	89	44
C_{12}	176	20	98
C_{13}	115	72	97
C_{15}		-3	-4
C_{23}		70	97
C_{25}		-26	4
C_{35}		16	27
C_{46}		-17	8

3.3.2 U_2MoSi , U_2ThSi_2 and $UNpSi$ electronic structure

Each of the three new phases are non-magnetic. Figures 14-16 show the electronic DOS and PDOS for U_2MoSi , U_2ThSi_2 and $UNpSi$. The occupied states at the Fermi level indicates each phase has metallic bonding. The three phases display similar features as seen in the GGA calculations for Np-Si phases (Figures 6 and 7), Pa_3Si_2 (Figure 12), and U-Si phases [5]. The f-orbital electrons for U and/or Np are the major contributor to the DOS at the Fermi level.

Figure 14. The a) total DOS and b) PDOS for U_2MoSi found from GGA calculations. The Fermi energy is set to 0 eV.

Figure 15. The a) total DOS and b) PDOS for U_2ThSi_2 found from GGA calculations. The Fermi energy is set to 0 eV.

Figure 16. The a) total DOS and b) PDOS for UNpSi found from GGA calculations. The Fermi energy is set to 0 eV.

4. Conclusions

We have presented DFT calculations for a number of actinide silicide systems. A goal of this work was to gain further insight into the complex bonding behavior of these materials and provide a comparison with previous work on U-Si phases. Structure prediction calculations were performed at select compositions to aid the construction of the convex hull in the Pa-Si and Np-Si systems. Additional structure searches at select U-Mo-Si, U-Th-Si and U-Np-Si compositions were attempted, which revealed dynamically and elastically stable U_2MoSi , U_2ThSi_2 and UNpSi phases.

Structure searches in the Np-Si system using GGA and GGA+D3 calculations revealed new structures for $NpSi_2$, NpSi, Np_3Si_2 and Np_2Si . These are crystallographically different from the experimentally observed structures and those found from previous work on the U-Si system [5]. Comparison of experimental and predicted electronic structure, magnetism and elastic properties among the structures show major differences. For example, the experimental structures are ferromagnetic, while predicted structures are non-magnetic. The use of GGA+ U stabilized the experimental structures with a U_{eff} larger than 0.8 eV. Additional experiments are warranted to further explore the discrepancies between the experimental and predicted Np-Si phases.

For the Pa-Si system, each of the phases have known structure-types. It was determined that GGA calculations may be sufficient to characterize the system,