Hafnium binary alloys from experiments and first principles

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Despite the increasing importance of hafnium in numerous technological applications, experimental and computational data on its binary alloys is sparse. In particular, data is scant on those binary systems believed to be phase separating. We performed a comprehensive study of 44 hafnium binary systems with alkali metals, alkaline earths, transition metals and metals, using high-throughput first principles calculations. These computations predict novel unsuspected compounds in six binary systems previously believed to be phase separating. They also predict a few unreported compounds in additional systems and indicate that some reported compounds may actually be unstable at low temperatures. We report the results for the following systems: AgHf, AlHf, AuHf, BaHf*, BeHf, BiHf, CaHf*, CdHf, CoHf, CrHf, CuHf, FeHf, GaHf, HfHg, HfIn, HfIr, HfK*, HfLa*, HfLi*, HfMg, HfMn, HfMo, HfNa*, HfNb*, HfNi, HfOs, HfPb, HfPd, HfPt, HfRe, HfRh, HfRu, HfSc, HfSn, HfSr*, HfTa*, HfTc, HfTl, HfV*, HfW, HfY*, HfZn, and HfZr (* = systems in which the ab initio method predicts that no compounds are stable).

High-throughput (HT) calculations of material properties based on density functional theory (DFT) have been developed in recent years for theoretically guided material discovery and improvement [1, 2, 3, 4, 5, 6, 7, 8]. These calculations give insights into trends in alloy properties and indicate possible existence of hitherto unobserved compounds. In this paper we apply the HT approach to a comprehensive screening of hafnium intermetallic binary alloys. This choice is motivated by the wide array of technological applications of hafnium alloys in contrast with their scant theoretical discussion in the literature.

Hafnium is primarily used in the control and safety mechanisms of nuclear reactors, because of its high cross-section for neutron absorption and its high corrosion resistance [9]. Hafnium cladding of nuclear fuel rods is expected to be an important element in the design of future advanced reactors [10]. Hafnium is used extensively as an alloying element in nickel-, niobium-, and tantalum-based superalloys, which are designed to withstand high temperatures and pressures. It is an important addition to some titanium, tungsten and molybdenum alloys, where it forms second-phase dispersions (with carbon) that improve material strength under extreme conditions [9, 11]. Hafnium alloys are also used in medical implants and devices, due to their biocompatibility and corrosion resistance (see for example [12]). Nickel-titanium-hafnium alloys exhibit shape memory behavior with high martensitic transformation temperatures and good mechanical properties [13]. Hafnium is added to aluminum-magnesium-scandium alloys, widely used in aerospace applications, to increase their strength following high temperature thermomechanical processing [14]. Some intermetallic compounds of Hf and the transition metals Fe, Co, Pd and Pt have been investigated as hydrogen-storage materials because of their capability to form hydrides with high hydrogen to metal ratios at room temperature [15].

Hafnium oxide based compounds have recently found wide application replacing silicon oxide as high-k dielectrics in the production of integrated circuits [16]. This has motivated a few first principles studies of the dielectric properties of hafnium silicates (see for example [17]). Perovskite alkaline metal hafnates (e.g. CaHfO3, BaHfO3 and SrHfO3) have been investigated for various optical and electronic applications as well as substrates for perovskite superconductor films, due to their high stability in the fabrication process of such films and their small crystallographic mismatch (see e.g. [18]). Although zirconium has been tried as a cheaper substitute for hafnium, in most of these applications only hafnium produces the desired properties [9].

Despite this wealth of existing and potential applications, computational studies of hafnium compounds are few. In most of these studies, just a few specific structures have been investigated [19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34]. In only three cases, Al-Hf, Cu-Hf and Hf-Nb [19, 34, 35, 36, 37], have a large number of structures been examined. In the Al-Hf system, the energies of 22 intermetallic structures have been calculated, four of which are ground states and constitute the convex hull of the system [33, 34] (The convex hull connects all of the ground states on a concentration vs. enthalpy diagram. The enthalpies of all other structures lie above the tie lines between the ground states. Thermodynamically, the convex hull represents the Gibbs free energy of the alloy at zero temperature [4]). In the Cu-Hf system, energies of 28 structures have been calculated and...
four identified as ground states. In both cases, differences have been found between the phase diagrams based on calorimetric measurements and the calculated ground states. In contrast, positive formation enthalpies were calculated for 13 Hf-Nb intermetallic structures, in agreement with experimental observations that the system is phase-separating.

In several systems, the stability of a few competing structures have been examined but the complete convex hull of the intermetallic system has not been addressed. These include the ground state properties of five different structures of Hf$_3$Mo, HfMo and HfMo$_3$ and the three Laves phases of HfCr$_2$, HfFe$_2$ and HfV$_2$. Single specific structures of Hf$_2$Fe, Hf$_2$Co, HfB$_2$, HfNi, Hf$_2$Ni, Hf$_2$Ru, HfRh, HfIr and HfPt have also been studied. Some of these compounds were studied because they are used in hyperfine field measurements by the time dependent perturbed angular correlation (TD-PAC) technique, for which $^{183}$Hf is an excellent probe, that can be easily compared to first principles calculations of the local electric field gradient in the vicinity of the probe.

In this paper we report a comprehensive computational study of the low temperature stability of 44 hafnium binary systems; hafnium combined with alkali metals, the alkaline earths, transition metals and metals. We apply the *ab initio* formation energy criterion which has been shown to be reliable for binary systems. The calculations were performed using the high-throughput framework AFLOW, employing *ab initio* calculations of the energies with the VASP software. We used projector augmented waves (PAW) pseudopotentials and the exchange-correlation functionals parameterized by Perdew, Burke and Ernzerhof for the generalized gradient approximation (GGA). The energies were calculated at zero temperature and pressure, with spin polarization, and without zero-point motion or lattice vibrations. All crystal structures were fully relaxed (cell volume and shape and the basis atom coordinates inside the cell). Numerical convergence to about 1 meV/atom was ensured by a high energy cutoff (40% higher than the highest energy cutoff for the pseudopotentials of the components) and dense 6000 k-point Monkhorst-Pack meshes. For each system, we calculated the energies of all the ground state structures reported in Refs. and about 200 additional crystal structures. In addition to the 176 structures described in, these included the prototypes A5, A6, A7, A11, B20, T1, ThIn, LiB-M51/2, Au$_3$Zr, Ca$_7$Ge, NbNi$_5$(P$_8$Ti), Ga$_2$Hf, W$_5$Si$_3$, V$_5$Zn$_5$, Ni$_2$Zr$_2$, C$_3$O and the complete set of hcp-superstructures with up to four atoms per cell.

Some of our results deviate from experimental data. Table is a summary of the alloy systems addressed in this study. On the first column, the alloying metals are ordered according to their Mendeleev number (or Pettifor's chemical scale). The reported experimental compounds (or lack thereof) are shown in the second column and the calculated ones in the third column. The compounds are presented with their structure designation or prototype in parentheses (unspecified or unknown structures are denoted as Unk.). Some of the predicted phases (marked by an asterisk) have structures for which no prototype is known and no Strukturbericht designation have been given. These new prototypes are described in Table. Appearance of two structures in the third column indicates their degeneracy. The fourth column gives the calculated energies of the structures identified on the convex hull of each binary system (3rd column). Energies of reported structures (2nd column) that are found to lie above the convex hull (missing in the 3rd column) are indicated in parentheses. In cases where the reported and calculated structures of a compound are different, or two non-degenerate structures are reported, the energy difference between them is indicated in square parentheses. The calculated convex hulls of all the compound forming systems are shown in Figs. (1)-(3).

In Table there are 16 systems that are reported in the literature as phase separating, i.e., having no compounds. 13 of these systems are grouped together at the top of the table. It is not surprising to see this same behavior in a block of the table, because the systems are listed by Pettifor’s Mendeleev number. The other three systems reported to be phase-separating, Hf-Mg, Hf-Tl and Hf-Pb, are scattered in the lower rows of the table. In these three cases, our calculations show that they are in fact compound forming, essentially complementing the general trend implied by the Pettifor chemical scale. Stable structures are also found in the binary systems of Hf with Ti and Zr (sharing the IVB column of the periodic table) and Sc. In five of the six systems predicted to be compound forming (excluding Hf-Pb) the pure elements have a hcp crystal structure and only disordered hcp solid solutions have been reported for their binary alloys with hafnium over the entire range of concentrations. The calculations indicate, however, that in four of them stable compounds that are *not* hcp-based superstructures should exist at low temperatures. Only in the Hf-Sc system, the new compounds are predicted to have a hcp based structure. Three of these metals have very high melting temperatures and the available experimental data on their alloys is also limited to high temperatures above 700°C, 800°C, 1000°C for Ti, Zr and Sc, respectively. No data is available for Hf-Mg, Hf-Tl and Hf-Pb alloys.
### TABLE I: Compounds observed in experiments or predicted by *ab initio* calculations in metallic binary alloys of Hf. Structure Strukturbericht designation or prototype are in parentheses (Unk. denotes unknown structures). New prototypes are marked by * and described in Table I. More than one structure may have been reported (2nd column) or found with degenerate energies (3rd column). ΔH are the formation enthalpies of the compounds in the present study; parentheses denote reported structures (2nd column) that lie above the convex hull (missing in the 3rd column). Square parentheses denote energy differences between experimentally observed and calculated structures or two reported non-degenerate structures.

| Compounds | ΔH (meV/at) |
|-----------|-------------|
| K,Na      | -           |
| Li,Na     | -           |
| Sr,Ca,Y   | -           |
| Sc        | -           |
| La        | -           |
| Zr        | -122       |
| Ti        | -11        |
| Nb, Ta    | -129       |
| V         | -120       |
| Mo        | -160       |
| W         | -160       |
| Cr        | -160       |
| Tc        | -160       |
| Re        | -160       |
| Mn        | -160       |
| Fe        | -160       |
| Os        | -160       |
| Ru        | -160       |
| Co        | -160       |
| Ir        | -160       |
| Rh        | -160       |
| Ni        | -160       |
| Pt        | -160       |

| Experiments | Calculations | ΔH |
|-------------|--------------|----|
| Hf₂Pd(C11S, C12S) | Hf₂Pd(C11S, C12S) | -527 |
| Hf₂Pd(UNK.) | Hf₂Pd(UNK.) | -682 |
| Hf₂Pd₄(UNK.) | Hf₂Pd₄(UNK.) | -817 |
| Hf₂Pd₃(C11S) | Hf₂Pd₃(C11S) | -879 [+11] |
| Hf₂Pd₄(D0₂₄, L1₂) | Hf₂Pd₄(D0₂₄, L1₂) | -635 |
| Hf₂Pd₅(Ptd₄T1) | Hf₂Pd₅(Ptd₄T1) | -430 |
| Au₄Hf(CuZr) | Au₄Hf(CuZr) | -414 |
| Au₄Hf₄(D0₄) | Au₄Hf₄(D0₄) | -483 |
| Au₄Hf₃(C11S) | Au₄Hf₃(C11S) | -565 |
| Au₄Hf₃(Cu₅T₁) | Au₄Hf₃(Cu₅T₁) | -563 |
| Au₄Hf₂(UNK.) | Au₄Hf₂(UNK.) | -545 |
| Au₄Hf₂(C11S) | Au₄Hf₂(C11S) | -440 |
| Ag₄Hf(CuZr) | Ag₄Hf(CuZr) | -119 |
| Ag₄Hf₄(D0₄) | Ag₄Hf₄(D0₄) | -122 |
| Cu₅Hf₁₄(Ag₅,Gd₁₄) | Cu₅Hf₁₄(Ag₅,Gd₁₄) | -139 |
| Cu₅Hf₃(Cu₅H₃) | Cu₅Hf₃(Cu₅H₃) | -173 |
| Cu₅Hf₃(Cu₅H₃) | Cu₅Hf₃(Cu₅H₃) | -186 |
| Cu₅Hf₂(C11S) | Cu₅Hf₂(C11S) | -166 |
| Cu₅Hf₂(C11S) | Cu₅Hf₂(C11S) | -166 |
| Mg₃Hg₄(Cd₄T₁) | Mg₃Hg₄(Cd₄T₁) | -7 |
| Hg₄Hg₅(CuZr) | Hg₄Hg₅(CuZr) | -120 |
| Cd₄Hf₄(CuZr) | Cd₄Hf₄(CuZr) | -88 |
| Cd₄Hf₄(CuZr) | Cd₄Hf₄(CuZr) | -87 [+18] |
| Zn₄Hf₃(CuZr) | Zn₄Hf₃(CuZr) | -175 |
| Zn₄Hf₃(CuZr) | Zn₄Hf₃(CuZr) | -233 [+18] |
| Be₃Hf₂(T₁₁₂) | Be₃Hf₂(T₁₁₂) | -173 |
| Be₃Hf₄(T₁₁₂) | Be₃Hf₄(T₁₁₂) | -223 [+485] |
| Be₃Hf₄(T₁₁₂) | Be₃Hf₄(T₁₁₂) | -226 |
| Be₃Hf₄(T₁₁₂) | Be₃Hf₄(T₁₁₂) | -166 |
| Be₃Hf₄(T₁₁₂) | Be₃Hf₄(T₁₁₂) | -75 |
| Hf₄In₅(T₁₁₂) | Hf₄In₅(T₁₁₂) | -145 |
| Hf₄In₅(T₁₁₂) | Hf₄In₅(T₁₁₂) | -285 |
| Al₄Hf₄(D0₂₄) | Al₄Hf₄(D0₂₄) | -356 [+9] |
| Al₄Hf₄(D0₂₄) | Al₄Hf₄(D0₂₄) | -415 |
| Al₄Hf₄(D0₂₄) | Al₄Hf₄(D0₂₄) | -398 |
| Al₄Hf₄(D0₂₄) | Al₄Hf₄(D0₂₄) | -374 |
| Al₄Hf₄(D0₂₄) | Al₄Hf₄(D0₂₄) | -314 |
| Al₄Hf₄(D0₂₄) | Al₄Hf₄(D0₂₄) | -277 |
| Al₄Hf₄(D0₂₄) | Al₄Hf₄(D0₂₄) | -252 |
| Al₄Hf₄(D0₂₄) | Al₄Hf₄(D0₂₄) | -224 |
| Ga₄Hf₄(D0₂₄) | Ga₄Hf₄(D0₂₄) | -382 |
| Ga₄Hf₄(D0₂₄) | Ga₄Hf₄(D0₂₄) | -456 |
| Ga₄Hf₄(D0₂₄) | Ga₄Hf₄(D0₂₄) | -664 |
| Ga₄Hf₄(D0₂₄) | Ga₄Hf₄(D0₂₄) | -519 |
| Ga₄Hf₄(D0₂₄) | Ga₄Hf₄(D0₂₄) | -495 |
| Ga₄Hf₄(D0₂₄) | Ga₄Hf₄(D0₂₄) | -445 |
| Ga₄Hf₄(D0₂₄) | Ga₄Hf₄(D0₂₄) | -404 |
| Pb₄Hf₄(WS₂) | Pb₄Hf₄(WS₂) | -253 |
| Sn₄Hf₄(WS₂) | Sn₄Hf₄(WS₂) | -380 |
| Sn₄Hf₄(WS₂) | Sn₄Hf₄(WS₂) | -396 |
| Sn₄Hf₄(WS₂) | Sn₄Hf₄(WS₂) | -270 |
| Sn₄Hf₄(WS₂) | Sn₄Hf₄(WS₂) | -265 |
| Bi₂Hf₄(WS₂) | Bi₂Hf₄(WS₂) | -147 [+14] |
| Bi₂Hf₄(WS₂) | Bi₂Hf₄(WS₂) | -166 |
| Bi₂Hf₄(WS₂) | Bi₂Hf₄(WS₂) | -182 |
| Bi₂Hf₄(WS₂) | Bi₂Hf₄(WS₂) | -169 |
FIG. 1: Formation enthalpies of Ag-Hf, Al-Hf, Au-Hf, Be-Hf, Bi-Hf, Cd-Hf, Co-Hf, Cu-Hf, Fe-Hf, Ga-Hf, Hf-Hg, Hf-In, Hf-Ir, and Hf-Mg alloys.
FIG. 2: Formation enthalpies of Hf-Mn, Hf-Mo, Hf-Ni, Hf-Os, Hf-Pb, Hf-Pd, Hf-Pt, Hf-Re, Hf-Rh, Hf-Ru, Hf-Sc, Hf-Sn, Hf-Tc, Hf-Ti, and Hf-Tl alloys.
that order, whereas the structure reported in the literature is C15 \[44\]. This is in agreement with the calculation in Ref. \[24\] that also found C14 as the lowest energy structure of these three Laves phases for HfV\(_2\). The compound HfV\(_2\) reported in the literature is therefore unstable at low temperatures. The discrepancy between the computational result of C14 as the minimum energy structure (Hf atoms on the sites of a hexagonal diamond structure) and the observed high temperature C15 phase (Hf on the sites of a diamond structure) may be due to vibrational stabilization at high temperature. In fact, C15 is only 24 meV/atom above C14, and given that entropic differences between structures can be of the order of 0.1-1.0k\(_B\) per atom \[50\], very small energy differences between the experimentally observed structure and our \textit{ab initio} results could be reversed at elevated temperature. The phenomenon is common, e.g. in Ref. \[51\] the vibrational entropy difference is shown to stabilize the \(\theta\)-Al\(_2\)Cu (C16) phase over the competing Al\(_2\)Cu-\(\theta'\) phase (distortion of \(\theta\)-C1), which has the lowest energy and is, therefore, stable at low temperatures.

In agreement with experimental data, all the other transition metals, from columns VIB to IIB of the periodic table, have stable compounds with hafnium at low temperatures. The situation is especially simple for the VIB metals, chromium, molybdenum and tungsten, for which the calculations confirm the existence of a single compound HfM\(_2\) with a C15 structure. Other Hf-Mo compounds for which \textit{ab initio} calculations have been previously performed \[20\] are shown to be unstable. The Hf-Hg system also exhibits a single compound, Hf\(_2\)Hg, where the calculations confirm that the reported structures C\(_{11b}\) \[43\] and CuZr\(_2\) \[44\] are degenerate.

The calculations for the Fe-Hf system show the existence of a stable compound Fe\(_2\)Hf with a C15 structure, and the C14 structure just slightly less stable (14 meV/atom). This is consistent with the literature where the two structures have been reported \[44\] at temperatures above 600\(^{\circ}\)C. However, in contrast to the available experimental data, the calculation shows that the compounds FeHf\(_2\) (B2 structure) and Fe\(_2\)Hf (C15\(_b\)) are also stable whereas the FeHf\(_2\) compound, reported with a NiTi\(_2\) structure, is unstable at low temperatures. Its formation energy is 35 meV/atom higher than the tie line FeHf(B2)\(\leftrightarrow\)Hf(A3) and thus could decompose at temperatures lower than 100\(^{\circ}\)C (Fig. 1). A similar behavior is found in the HfMn system where the C14 structure of HfMn\(_2\) is found to be stable, with the C36 and C15 structures at slightly higher energies (4 and 5 meV/atom, respectively). The experimentally reported Hf\(_2\)Mn compound (NiTi\(_2\) prototype), is again found to be unstable at low temperatures, at 30meV/atom above the Hf(A3)\(\leftrightarrow\)HfMn\(_2\)(C14) tie line.

In the Hf-Ru and Hf-Os systems, a stable B2 structure of HfRu and HfOs is found in agreement with the experiments \[44\]. The compounds Hf\(_2\)Os, Hf\(_{54}\)Os\(_{817}\)
and HfO$_2$ reported from experimental data are found to be unstable. No stable structure was found for the HfRu compound, whose existence was suspected in some experiments [14]. In the Hf-Re system ref. [14] reports a Hf$_2$Re$_{25}$ compound (prototype Re$_2$Zr$_2$) whereas ref. [33] reports a HfRe compound of unspecified prototype. Our calculations confirm the existence of the Hf$_2$Re$_{25}$ compound but find no stable structure for HfRh. The lowest HfRh structure, B$_2$, lies approximately 50meV/atom above the convex hull (Table I and Fig. 2). For the Co-Hf system, our calculations confirm the existence of the stable compounds Co$_2$Hf, CoHf, and CoHf$_2$ at low temperatures, albeit with structures different from those reported in experiments. The reported Ni$_2$Zr$_2$ structure of Co$_2$Hf lies above the convex hull (Table I and Fig. 1).

The Cu-Hf system is the only transition metal-hafnium system previously studied by ab initio methods, also using the VASP software but with different potentials than in our study (Vanderbilt-type ultrasoft pseudopotentials) [37]. 28 different compound structures have been calculated, of which four, Cu$_3$Hf, Cu$_6$Hf$_3$, Cu$_{10}$Hf$_7$ and CuHf$_2$ were identified as stable. Our calculations also indicate that these four compounds are stable. There is no experimental information about the structure of Cu$_5$Hf [44]. We obtain the AuBe$_3$ structure in agreement with ref. [37]. The CuZr$_2$ structure, reported in experiments for CuHf$_2$ [44], and not calculated in ref. [37] is degenerate with the reported C11$_b$ structure. The ground state convex hull is asymmetric and skewed towards the Cu side, in agreement with the general conclusions of ref. [37] (Fig. 1). The Al-Hf system was studied using the same methodology [35]. The convex hull in this case is defined by four compounds Al$_3$Hf(D0$_{23}$), Al$_2$Hf(C14), Al$_3$Hf$_4$(Al$_3$Zr$_4$) and AlHf$_3$(L1$_2$), with Al$_5$Hf$_2$(Al$_3$Zr$_2$) and AlHf$_3$(B33) slightly above the convex hull. Our calculations reproduce these results and show in addition that the AlHf structure TII, reported in the experimental data but not studied in Ref. [35], is degenerate with B33. Other compounds reported for this system [44] are found to be significantly above the convex hull and should therefore be unstable at low temperatures (see Table I and Fig. 1).

Our HT study uncovers a few compounds on which no data is available in the experimental literature [43, 44] in the binary systems of Hf with Au, Bi, In, Pd, Pt, Re, and Tc. A few reported compounds are found to lie above the convex hull of their respective systems (Hf with Be, Ga, Ni and Sn) and are thus predicted to be unstable at low temperatures. (Table I).

In most cases where two structures are reported in the experimental literature, the calculations show that they are indeed degenerate or the energy differences are small, 30 meV/atom or less (square parentheses in Table I). In only two cases these structures differ considerably. The B2 structure of HfPt is 165meV/atom higher than the degenerate B33/TII groundstate. No phase diagram is available for the Hf-Pt system, but the experimental data indicates that the B2 structure might have been observed in a non-stoichiometric mixture [43]. The calculations seem to provide an indirect confirmation of this observation, showing that B2 is not a stable structure of the stoichiometric mixture. The Th$_2$Ni$_{17}$ structure of Be$_{17}$Hf$_2$ is 485meV/atom higher than the Th$_2$Zr$_{17}$ groundstate (sometimes also denoted as Be$_{17}$Nb$_2$ [43, 44]). As discussed in Ref. [37], it has not been determined whether Be$_{17}$Hf$_2$ consists of both forms or just one of them. The large energy difference obtained in our calculations indicates that one structure is much more likely than the other and the compound should consist exclusively of the Th$_2$Zr$_{17}$ prototype.

In conclusion, a systematic and comprehensive ab initio study of phase stability is carried out for the hafnium intermetallic systems. The total energies of about 200 intermetallic compounds have been calculated for 44 hafnium-metal systems and some interesting deviations from published experimental data were found. In particular, the calculations predict the existence of stable compounds in six hafnium intermetallic systems previously believed to be phase-separating. On the Pet-tifor chemical scale, three of these are isolated phase-separating systems in a cluster of compound-forming ones, and the discrepancy is likely due to lack of experimental data. Hence, these predictions nicely complement the trend indicated by the empirical scale. A few new compounds are predicted in binary systems of Hf and other metals, and some compounds reported in the literature are shown to be unstable at low temperatures.

A detailed understanding of Hf alloys is crucial for a better realization of its potential as an alloying agent in currently available applications and in developing new ones. The picture of Hf alloys that emerges from this study is quite different from that depicted by current experimental data. It should be emphasized that we consider the alloys to be in thermodynamical equilibrium, which can be difficult to reach at low temperatures due to slow kinetics. At higher temperatures, configurational disorder and vibrational entropic promotion might destabilize the predicted compounds. The theoretical predictions presented here should therefore motivate research for their experimental validation and provide useful guidance to future studies of these alloys.

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| System        | Hf₂Sc⁺ | Hf₂Sc⁺ | BiH₂⁺ | Mo₅Ti⁺ | Hf₅Pb⁺ | HfP₄⁺⁴⁺ |
|---------------|--------|--------|--------|--------|--------|--------|
| Superlattice  | HCP As₂B₂ | HCP As₂B₁ | HCP As₂B₄ | BCC AB₃ | FCC As₂B₁ | none |
| Lattice       | Orthorhombic | Hexagonal | Monoclinic | Orthorhombic | Tetragonal | Orthorhombic |
| Space Group   | Cmcm #63 | P6₂m #189 | C2/m # 12 | Immm #71 | P4/nmm #123 | Cmmn #65 |
| Pearson symbol| oC16   | hP6    | mC12   | oI8    | oP6    | oC12   |
| Primitive vectors (cart.) | | | | | | |
| a₁/a         | (2, 0, 0) | (3/2, −√3/2, 0) | (3/2, −√3/2, 0) | (3/2, 1/2, −1/2) | (1/2, 1/2, 0) | (−2.01059, 5.93236, 0) |
| a₂/a         | (1, √3, 0) | (3/2, 3√3/2, 0) | (1, √3/2, −√3) | (1/2, 3/2, 1/2) | (0, 3, 3) | (−2.01059, −5.93236, 0) |
| a₃/a         | (0, 0, √3/2) | (0, 0, √3/2) | (0, √3 − √3/2) | (−1/2, −3/2, 1/2) | (1/2, 5/2, 3) | (0, 0, 4.02718) |
| Atomic positions (fract.) | | | | | | |
| A₁           | (0, 0, 0) | (0, 0, 0) | (0, 0, 0) | (0, 0, 0) | (0, 0, 0) | (0.02752, 0.97247, 0) |
| A₂           | (0, 1/2, 0) | (1/3, 0, 0) | (7/18, 7/15/18) | (0, 0) | (0, 1/6, 0) | − |
| A₃           | (1/2, 0, 0) | (0, 0, 0) | − | − | (0, 1/3, 0) | − |
| A₄           | (1/6, 1/6, 1/2) | (1/3, 0, 1/2) | − | − | (0, 1/2, 0) | − |
| A₅           | (1/6, 2/3, 1/2) | (1/3, 1/3, 1/2) | − | − | (0, 2/3, 0) | − |
| A₆           | (2/3, 1/6, 1/2) | − | − | − | − | − |
| B₁           | (1/2, 1/2, 0) | (1/3, 2/3, 1/2) | (1/3, 2/3, 2/3) | (1/4, 3/4, 1/2) | (0, 5/6, 0) | (0.19430, 0.80569, 0.5) |
| B₂           | (2/3, 2/3, 1/2) | − | (2/3, 1/3, 1/3) | (1/2, 1/2, 0) | − | (0.36452, 0.65347, 0) |
| B₃           | − | − | (13/18, 4/9, 17/18) | (3/4, 1/4, 1/2) | − | (0.52795, 0.47204, 0.5) |
| B₄           | − | − | (1/18, 1/9, 11/18) | − | − | (0.69061, 0.39938, 0) |
| B₅           | − | − | − | − | − | (0.86173, 0.13826, 0.5) |

TABLE II: Geometry of new prototypes in our study. Positions are given as unrelaxed positions in the parent lattice.

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