Finding the stable structures of $N_{1-x}W_{x}$ with an *ab initio* high-throughput approach

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Using density functional theory calculations, many researchers have predicted that various tungsten nitride compounds $N_{1-x}W_{x}$ ($x < \frac{1}{2}$) will be “ultraincompressible” or “superhard,” i.e., as hard as or harder than diamond. Necessary conditions for such compounds are that they have large bulk and shear moduli, greater than approximately 200 GPa, and are elastically and vibrationally stable. Compounds with such desirable properties also must be energetically stable against decomposition into other compounds. This test for stability can only be found after the determination of the convex hull for $N_{1-x}W_{x}$, which connects the lowest enthalpy structures as a function of composition. Unfortunately, the experimental phase diagram of the N-W structure is uncertain, as it is difficult to break the $N_2$ bond to form compounds with tungsten. Experiment also indicates that there are a large number of partially filled sites in most N-W structures. This introduces computational difficulties since we cannot easily model randomly placed vacancies. In addition, van der Waals forces play a significant role in determining the structure of solid $N_2$ and the nitrogen-rich compounds. This makes it difficult to determine the relative energies of these compounds, as there is no universally accepted density functional incorporating van der Waals interactions. The exact shape and even composition of the convex hull is dependent upon the choice of density functional, even if we only chose between the local density approximation and a generalized gradient functional. Despite these difficulties, computations can determine much about the ground-state form of the convex hull. Here, we use high-throughput calculations to map out the hull and other low-energy structures for the N-W system. The lowest-energy structures all have vacancies, on the tungsten sites in hexagonal-based compounds, and on both the nitrogen and tungsten sites in cubic compounds. We find that most of the N-W structures proposed in the literature, both theoretical and experimental, are above the convex hull, in some cases by over 0.2 eV/atom. One of the ground-state phases, N-W in the NbO structure, has relatively large bulk (>300 GPa) and (>200 GPa) shear moduli, and so is a candidate superhard material. This will require further investigation.

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I. INTRODUCTION

One of the major goals of electronic-structure calculations is the prediction of crystal structures as a function of composition [1–3]. Determining the possible configurations of a compound as a function of composition is the first step in determining its material properties at equilibrium. It is also likely that any pressure- or temperature-driven phase transitions will be from the equilibrium structure to another structure which is close to it in energy and composition. Such calculations are of particular interest when there is little known about the system theoretically.

There are a variety of mechanisms for this: searching over a wide range of known [4] and likely [5] structures for the material in question, searches starting from randomly positioned atoms [6], and even structures predicted from apparently “out of the blue” [7]. In the end these techniques produce a set of metastable structures, all of which have zero force on the atoms in the crystal, zero stress, and no imaginary phonon modes. Some structures will be stable, that is, it is not energetically favorable for them to decompose into other structures.

When searching for stable structures, this last point is key. We can find the lowest-energy structure of, e.g., composition $A_2B_3$, but we cannot tell if it is truly stable until we show that it cannot decompose into $2A + 5B$, or $A_2B_2 + 3B$, or some other combination of structures. In other words, to completely determine structural stability of a compound, we must search over all possible compositions.

Once this is done there is still the question of whether or not we have done the appropriate calculation. Most electronic-structure calculations are done using the Kohn-Sham *ansatz* [8] to density functional theory (DFT) [9]. Since the exact density functional is not known, we necessarily use approximate forms. It is not *a priori* certain that the local density approximation (LDA) [10,11] will give the same results as a generalized-gradient functional such as Perdew-Burke-Ernzerhof (PBE) [12]. If van der Waals forces...
Using density functional theory calculations, many researchers have predicted that various tungsten nitride compounds N\(1-x\)W\(x\) (\(x < 1.2\)) will be ultra-incompressible or superhard, i.e., as hard as or harder than diamond. Necessary conditions for such compounds are that they have large bulk and shear moduli, greater than approximately 200 GPa, and are elastically and vibrationally stable. Compounds with such desirable properties also must be energetically stable against decomposition into other compounds. This test for stability can only be found after the determination of the convex hull for N\(1-x\)W\(x\), which connects the lowest enthalpy structures as a function of composition. Unfortunately, the experimental phase diagram of the N-W structure is uncertain, as it is difficult to break the N2 bond to form compounds with tungsten. Experiment also indicates that there are a large number of partially filled sites in most N-W structures. This introduces computational difficulties since we cannot easily model randomly placed vacancies. In addition, van der Waals forces play a significant role in determining the structure of solid N2 and the nitrogen-rich compounds. This makes it difficult to determine the relative energies of these compounds, as there is no universally accepted density functional incorporating van der Waals interactions. The exact shape and even composition of the convex hull is dependent upon the choice of density functional, even if we only chose between the local density approximation and a generalized gradient functional. Despite these difficulties, computations can determine much about the ground-state form of the convex hull. Here, we use high-throughput calculations to map out the hull and other low-energy structures for the N-W system. The lowest-energy structures all have vacancies, on the tungsten sites in hexagonal-based compounds and on both the nitrogen and tungsten sites in cubic compounds. We find that most of the N-W structures proposed in the literature, both theoretical and experimental, are above the convex hull, in some cases by over 0.2 eV/atom. One of the ground-state phases, N-W in the NbO structure, has relatively large bulk (>300 GPa) and (>200 GPa) shear moduli, and so is a candidate superhard material. This will require further investigation.
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are important, we should use some variety of van der Waals–
enabled functional [13]. If multiple functionals for a given
system predict the same stable structures and compositions,
then it is likely that these compounds will form. If different
functionals produce different results, then we cannot decide
the issue on the basis of current density functional theory and
must appeal to more accurate techniques or to experiment.

As an example, we look at tungsten nitrogen system. There
are many experimental studies showing evidence of stable
$N_{1-x}W_x$ compounds [14–21], and there is no assessed phase
diagram diagram available [22]. Indeed, until recently [21] it
was very difficult to make nitrogen-rich $N_{1-x}W_x$ compounds
since tungsten does not dissolve appreciable amounts of $N_2$
[23]. In addition, above 600 $\degree$C the compound usually referred
to as tungsten nitride decomposes to NW$_2$, which itself loses
nitrogen above 1000 $\degree$C [23].

Tungsten carbide is of interest as a structural material, or at
least a coating, because of computational studies which claim
that some compounds $N_{1-x}W_x$ with $x < \frac{1}{2}$ are “superhard”,
or at least have very stiff elastic constants and so are superhard
candidates [24–30].

While all these calculations show that the favored phase
of $N_{1-x}W_x$ is stable against decomposition into $N_2$ and
tungsten, none provide a detailed calculation of the possible
stable and metastable structures of $N_{1-x}W_x$ as a function of
tungsten concentration $x$. It is thus difficult to determine if
these structures will form experimentally, or to determine if
structures which do form are stable or only metastable.

Our original motivation for this study was the possibility that
$N_xW$ (or $N_{0.5}W_{0.5}$) might be a superhard metal [30]
and can be in fact easily fabricated. As noted above, this
requires knowledge of the entire equilibrium phase diagram
for $N_{1-x}W_x$. We did this using AFLOW [31], a high-throughput
front end for electronic-structure calculations [1]. AFLOW
allows us to quickly examine a selected range of structures
using high-performance supercomputers and modern den-
sity functional electronic-structure techniques. The AFLOW
prototype database, which was originally used to describe
intermetallic alloys [32–36], can easily be enlarged [37]. We
were therefore able to include ionic and covalent structures
for systems similar to N-W. These include borides, carbides,
oxides, and other nitrides. We also invented many structures
to mimic the random pattern of vacancies on both the tungsten
and nitrogen sites that have been observed under experimental
conditions.

AFLOW allows the use of a variety of different density
functionals. We did our primary calculations using the Perdew–
Burke-Emzerhof (PBE) generalized-gradient functional [12].
For low-energy systems we also used the local density approx-
imation [10,11] (LDA). We also approximated van der Waals
forces, which are important in nitrogen-rich structures, using
the vdW–DF2 functional [38]. As we shall see, predictions
for ground-state structures are strongly dependent on the choice
of functional.

Here, we are searching for structures of composition
$N_{1-x}W_x$ which are stable, or are metastable with a reasonable
probability of being found experimentally. A metastable
compound must be vibrationally stable, i.e., have no imaginary
phonon frequencies as well as elastic constants which satisfy
the Born criteria [39]. True stability requires an additional

\[ \Delta H(N_xW_y) = [E(N_xW_y) - B E(W)] - \frac{1}{2} A E(\alpha N_2)/(A + B) < 0, \]

where $\Delta H(N_xW_y)$ is the formation energy per atom
of a compound with this stoichiometry, $E(N_xW_y)$ is the
energy/formula unit of the compound, $E(W)$ is the equilibrium
energy per atom of body-centered-cubic tungsten, and $E(\alpha N_2)$
is the equilibrium energy per molecule of solid $\alpha N_2$. $\Delta H$ will
be negative if it is energetically possible for the compound to
be formed spontaneously from solid $N_2$ and $W$. The compound
will be completely stable if it is not energetically favorable for
it to decompose into any other N-W compound. This requires
that the compound be on the convex hull determined from the
plot of $\Delta H$ versus tungsten concentration $x = N/(M + N)$
over all possible compounds in the system [42].

The purpose of the paper is to determine $\Delta H$ for a
sufficient number of N-W compounds so that we have a
good approximation to the shape of the convex hull and the
structures forming it, and to determine the electronic, elastic,
and vibrational properties of compounds on or near the convex
hull, looking for superhard candidates. An estimate of the
actual hardness of these materials is beyond the scope of this
paper, but in general will follow the procedures in Ref. [30].

The paper is organized as follows. Experimental and previ-
ous theoretical work is shown in Sec. II. Our computations
are described in Sec. III. Our results are shown in Sec. IV, which
is broken up into several subsections, including $\beta$ (cubic)
and $\delta$ (layered hexagonal) compounds, compounds containing
$N_2$ dimers, compounds resembling SiO$_2$, and miscellaneous
structures. Finally, we discuss our results in Sec. V.

Our study of tungsten nitride required searching over a
large number of known experimental structures [43–47], and
even inventing structures which had vacancy patterns related
to those seen experimentally. The Supplemental Material [48]
contains crystallographic information for 108 of the lowest-
energy structures, along with additional computational details.
In all, we studied over 500 structures using the high-throughput
AFLOW platform. Structural parameters for these additional
structures are available on request.

We always refer to the composition of tungsten nitride in
the form $N_{1-x}W_x$, where $x$ is the atomic fraction of tungsten,
or, for stoichiometric compounds, $N_xW_y$, where $A$ and $B$
are integers. Various other authors reverse the order of these
compounds, e.g., “r-W$_2N_3” [21]. To avoid confusion, we place
these designations in quotes. In the Supplemental Material
[48], all structures are ordered by tungsten concentration $x$.

II. EXPERIMENTAL AND THEORETICAL BACKGROUND

Wriedt [22] summarizes the experimental N-W data known
before 1990. The cubic $\beta$ phase is essentially the face-
centered-cubic NaCl structure (structure #67 in the Supple-
mental Material [48]), with vacancies on the nitrogen site
leading to compounds of the form $N_{1-x}W_x$ with $x > \frac{1}{2}$. The
cubic lattice constant for all of these phases is approximately
4.13 Å. These structures were originally studied by Hägg [14], and later by Khitrova and Pinsker [17–19]. Kiessling and co-workers [15,16] found a similar phase which they designated γ. This structure also seems to be related to the NaCl structure, but with $x \approx 1$.

The hexagonal δ phase structures were extensively studied by Khitrova and Pinsker [18,19]. They defined six distinct crystallographic structures $\delta_1$ and $\delta_4$, which we will discuss in more detail in the following. Compositions $\text{N}_1-x\text{W}_x$ are said to range from $x = 0.33$ to 0.67. As NaCl is the base structure for the β phase, we can consider tungsten carbide [49] (structure #61 in the Supplemental Material [48]) as the basis for most of the δ phase structures. These structures are composed of stacked triangular planes of tungsten or nitrogen atoms. Unlike the β phases, vacancies appear only in the tungsten planes.

In addition to bulk structures, Shen and Mai [50] have grown thin-film N-W films. They found some evidence of the β phase at NW$_2$, but most of the films were amorphous.

These compounds are difficult to make and to stabilize. As noted by Toth [23], “tungsten does not dissolve appreciable amounts of nitrogen as a terminal solid solution,” and must be formed at temperatures under 800°C. Recently, however, Wang, Yu, Lin et al. [21] (hereafter referred to as WYL+) were able to use solid-state ion exchange and nitrogen degassing under pressure to produce several tungsten nitride phases with compositions ranging from $\text{N}_2$ to $\text{N}_8$ ($0.4 \leq x \leq 0.6$). Although they do not state this, all of these structures can be classified as either β-NW or δ-NW, as defined above. We will have more to say about these structures as we discuss our computational results.

Computational studies of the tungsten-nitride system followed in the wake of the development of high-speed computers and computationally efficient density functional codes. We will discuss some of these papers in more detail in the next section. For now, we briefly describe their results. These researchers studied specific crystal structures of tungsten nitride, but none have examined structures over a large range of compositions.

Kroll, Schröter, and Peters [24] considered the nickel arsenide structure [51] (structure #59 in the Supplemental Material [48]) to be the ground state of NW. They also looked at several possible structures for $\text{N}_2\text{W}_2$, including babdelelyte [52] (#20), which they found to have the lowest energy, brookite [53] (#18), and cotunnite [54] (#23), which they found to be a high-pressure (~35 GPa) phase of $\text{N}_2\text{W}$.

Suetin, Shein, and Ivanovski [25] modeled tungsten nitride by assuming it to be in either the tungsten carbide (WC, #61 in the Supplemental Material [48]) or the sodium chloride (NaCl, #67) structure. They computed elastic constants, isotropic bulk moduli in the Reuss and Voigt approximations [55], and the corresponding isotropic Young’s modulus and Poisson’s ratio. The NaCl structure is elastically unstable, with $C_{44} < 0$. The WC compound, on the other hand, was found to be rather stiff, with a shear modulus of about 150 GPa. The enthalpy $\Delta H$ was not calculated, so there could be no estimate of stability against dissociation into $\text{N}_2$ and bcc tungsten.

Wang, Li, Li, Xu et al. [26] (hereafter WLLX+) used an evolutionary method to find two related $\text{N}_2\text{W}$ structures (#11 and #12) which had shear moduli > 200 GPa. These structures, which consisted of vertically aligned $\text{N}_2$ dimers alternating with hexagonal tungsten planes, have $\Delta H < 0$, as well as elastic constants satisfying the Born criteria [39]. In addition, both structures are insulators, with a band gap on the order of 1 eV.

Benhai, Chunlei, Xuanyu, Qiuju, and Dong [27] looked at the elastic behavior of a variety of NW ($x = \frac{1}{2}$) structures, at pressures up to 100 GPa. They found that the NiAs structure was preferred over the WC at all pressures. They did not calculate the change in enthalpy relative to the $\text{N}_2$ and bcc W end points, nor did they consider some of the lower-energy structures we report in the following.

Song and Wang [29] studied NW in the WC structure, $\text{N}_2\text{W}$ in the CoSb$_3$ structure (#20, although they refer to it as IrP$_2$), and $\text{N}_3\text{W}$ in the P$_3$Tc structure [56] (#10), using the LDA functional. They found a negative value of $\Delta H$ for all three compounds, although it is not clear what reference point they used for pure nitrogen. In all cases, they found shear moduli below 200 GPa but bulk moduli greater than 300 GPa.

Suetin, Shein, and Ivanovski [57] modeled $\text{N}_2\text{W}$ in what we believe to be the CTi$_2$ structure [58], a cubic supercell of the NaCl structure with ordered vacancies on one of the sublattices (see structure #95 in the Supplemental Material [48]). This is an approximation to the cubic NW phase found by Hägg [14]. Although they compared the electronic structure to that found for the WC and NaCl structures in their earlier paper [25], they give no information about the stability of this structure.

Du, Wang, and Lo [28] looked at a tetragonal analog (#26) to the hexagonal structures found by WLLX+. They found it to be stable compared to these structures above 150 GPa, but never stable compared to the cotunnite structure (#23). Li, Zhai, Fu et al. [59] computed the pressure dependence of the elastic constants of these structures, and found that both are elastically stable up to pressures of 200 GPa.

In addition to their experimental work, WYL+ [21] also used first-principles calculations to determine the elastic constants of the three stoichiometric structures they studied, as well as what they call the c-BN structure (actually zinc-blende [60–62] #65). Bulk moduli all exceed 350 GPa, and shear moduli are estimated at around 180 GPa, but reach 390 GPa for the c-BN structure. They did not otherwise discuss the possible stability of these phases.

Aydin, Ciftci, and Tatar [30] (hereafter ACT) modeled $\text{N}_2\text{W}$ using the starting point of the ReP$_3$ structure [63] (#7). They found this structure to be mechanically stable, and $\Delta H < 0$. The shear modulus of this structure was approximately 200 GPa, and they estimated the hardness of the material to be on the order of c-BN. If it could be made, then, it would most likely be a superhard material. We will discuss our findings for this structure in detail in the following.

Zhang, Yan, Wei, and Wang [64] calculated the equilibrium lattice parameter and elastic constants of WYL+’s “c-W$_3\text{N}_4$” structure [21], which has the prototype [65] $\text{Si}_2\text{U}_3$ (#47). Later Liu, Wang, Zhou, and Chang [66] looked at the pressure dependence of the elastic constants and phonon frequencies of the same structure. This structure has very large bulk and shear moduli, but we shall see that it is far above the convex hull of the tungsten nitride phase diagram.

Liu, Zhou, Gall, and Khare [67] recently computed the elastic constants of transition-metal nitrides in the NbO structure [68]. Their calculation for NW showed it to be very...
stiff, with its bulk modulus over 300 GPa and the shear modulus above 200 GPa. We will discuss this structure further below.

Summarizing the experimental and theoretical results, we find that the low-lying structures of tungsten nitride fall into one of five classes, the first two roughly corresponding to structures discussed by Schönberg [49]:

1. $\beta$ phases. These structures are supercells of the cubic NaCl structure (#67 in the Supplementary Material [48]). Removing atoms from the supercells generally leads to a lower-energy cell. Examples are the $\text{S}_3\text{U}_4$ structures (#47 and #78), which have either one N or one W vacancy in an eight-atom supercell, the NbO [68] (#53) structure, which has second-neighbor N and W vacancies, and the $\text{CTI}_2$ structure [58] (#95), which approximates the NW$_2$ $\beta$ phase found by Hägg [14]. For our purposes we will treat the similar $\gamma$-NW structure [15,16] as part of the $\beta$ phase.

2. $\delta$ phases. In general these are hexagonal or trigonal unit cells containing alternating triangular planes of nitrogen and tungsten. The tungsten planes generally contain vacancies [18,21]. The experimental composition of these phases ranges from about [21] $\text{N}_2\text{W}_3$ to NW$_2$ [18].

3. $\text{N}_2$ phases. In these structures the N$_2$ molecules stay intact, possibly within a tungsten matrix. The only experimental examples we have of these phases are the several varieties of solid N$_2$ [40]. Computation have found structures with composition N$_2$W (Ref. [26], #11 and #12) and N$_2$W (Ref. [30], #7) that appear to be at least metastable.

4. SiO$_2$ phases. These have not been seen experimentally, and are only exceptionally low in energy when using the vdW–DF2 van der Waals functional. In these structures, the nitrogen atoms form a tetrahedron around each tungsten atom, and each nitrogen bonds with two tungsten atoms. A number of such structures appear in the literature [69]. Here, we examine a few of the more common ones.

5. Miscellaneous structures. This category includes those structures which do not fit into one of the categories defined above, including a derivative of the FeB$_4$ compound proposed by Van der Geest and Kolmogorov [70] (#8), and the surprisingly low-energy MoS$_2$ structure (#89). None of these have been seen experimentally.

III. METHODS

We began our search for the convex hull of the N-W system by using AFLow [1,31,71] to quickly and efficiently search through a large database of structures. As the original AFLow prototype database was for binary metallic alloys [32–36], we have extended it to include over 100 new structures. These include nitrides, oxides, borides, and carbides, as well as supercells of standard structures with atoms removed to mimic the random patter of vacancies seen experimentally. The crystallographic information for the important structures, including all of those discussed in Secs. II and IV are described in the Supplemental Material [48].

Electronic-structure calculations were done using the Vienna ab initio simulation package (VASP) [72,73], including core-state effects via the VASP implementation [74] of the projector augmented-wave (PAW) method [75].

AFLow’s default is to use the Perdew–Burke–Ernzerhof (PBE) implementation [12] of the generalized-gradient approximation (GGA) to density functional theory (DFT) [8,9]. There are, however, substantial differences, especially in the estimates of enthalpy changes, between PBE results and those from the LDA [10,11]. This was shown by WLLX+ [26], and we shall see further examples in the following. Accordingly, we calculated the convex hull using both LDA and PBE functionals within VASP.

We used the VASP-supplied LDA and PBE PAW potentials for nitrogen and tungsten (specifically, May 2000 LDA and April 2002 PBE PAW potentials for N, and the July 1998 LDA and September 2000 tungsten W-pv PAWs). All calculations use a kinetic energy cutoff of 560 eV, which is 40% larger than the suggested cutoff for nitrogen (400 eV). Unless otherwise stated, we let the AFLow package determine the k-point mesh for each structure. This is usually set to use approximately the same density of k points in reciprocal space for all structures.

Since there are a wide variety of structures in this system, both metallic and insulating, we made sure that the k-point mesh was dense enough to determine the electronic-structure energy to better than 1 meV/atom. For the NaCl structure, e.g., a $15 \times 15 \times 15$ Monkhorst-Pack grid [78] was originally used. For Wang et al.’s P6m2 N$_2$W structure, we used a $15 \times 15 \times 9$ mesh.

In the initial VASP calculations performed via AFLow, all structures are considered to be spin polarized, but the starting magnetization vanished as self-consistency was reached. The final calculations were all done assuming no moment.

The MedeA® software system [79] was used to drive VASP in calculations of the phonon spectra and for some other calculations. Elastic constants were computed by taking finite strains [80,81] and determining the slope of the corresponding stress-strain curve (as implemented in the MedeA® package, or using the native VASP option). Phonon frequencies were determined via the frozen-phonon approximation using the MedeA® package.

IV. COMPUTATIONAL RESULTS

The surprising thing about our computational work is that so little of it agrees with either the experimental or theoretical work discussed above. This section details our results, using three different density functionals. In the next section, we will discuss the disagreement between these results and previous work.

We computed the enthalpy of formation $\Delta H$ [Eq. (1)] for over 500 $\text{N}_1$–$\text{W}_x$ structures using the AFLow mechanism for high-throughput calculations, with VASP as our computational engine [72,73,82]. We used the PBE density functional [12] as our screening tool, but for “interesting” structures, i.e., structures within approximately 0.2 eV of the tie line, we also looked for the minimum energy structure using the LDA
N3 structure, which is one of two proposed structures are described by Donohue [40] and Mills, Oligner, and Cromer [83], comprising structures #1–#5 in the Supplemental Material [48] tables. We ignore the higher-energy nonmolecular structures of nitrogen such as cg-N [84], considering only solid N2 crystals, where the molecules are bound by their mutual van der Waals attraction [76]. Since LDA and PBE do not explicitly include long-range van der Waals forces, we might expect some difficulty in describing the ground state.

Table 1 shows the calculation of the equilibrium structure of αN2 in the Pa3 structure, which is one of two proposed structures. The equilibrium lattice constant and bulk modulus were determined by fitting energy versus volume data to a third-order Birch fit [86] and the internal parameter x was determined by minimizing the forces on the atoms at fixed lattice constant [87]. While all three functionals correctly determine the N2 bond length at 1.10 Å, none does particularly well in determining the equilibrium lattice constant and bulk modulus.

All N2 structures are essentially degenerate, differing by no more than 0.03 eV per atom as we go from αN2 to eN2. Thus current versions of DFT and electronic-structure algorithms, even including van der Waals interactions, cannot accurately determine the ground state of N2. We will study this in more depth in a future paper, but for now we will simply note that DFT calculations for pure nitrogen, and presumably for nitrogen-rich compounds, differ considerably depending on the choice of functional. One consequence of this is that the minimum entropy for this system ranges from −0.35 to −0.75 eV/atom, depending on the choice of functional.

Tungsten is naturally found in two forms [41], α–W (#106), the ground-state body-centered-cubic structure, and β–W (#107), commonly referred to by its Strukturbericht [43] designation A15. For this calculation we also considered [10,11] and vdW–DF2 [38] functionals. We also included all of the stoichiometric structures, both experimental and theoretical, from Sec. II. In the case of experimental structures with randomly ordered vacancies, we constructed supercells of the base structure, removing nitrogen and/or tungsten atoms as needed to reach the desired composition. This resulted in many high-energy structures which we will not describe further, but the procedure also found structures which shape the convex hull of the energy diagrams.

The resulting phase diagrams for these 108 structures are shown in Figs. 1 (LDA functional), 2 (PBE functional), and 3 (vdW–DF2 functional). The diagrams are decidedly different, especially for tungsten concentrations x < 0.4. The shape, depth, and even composition of the convex hull changes as we move from LDA to PBE to vdW–DF2 functionals. Differences between functionals will be discussed in the comments on the individual structures, below.

In the following, we describe in detail the most interesting of the 108 structures listed in the Supplemental Material [48], paying particular attention to how our predictions change with change in the choice of density functional.

#### A. End points of the phase diagram

First consider the end-point structures: The lowest-energy N2 structures are described by Donohue [40] and Mills, Oligner, and Cromer [83], comprising structures #1–#5 in the Supplemental Material [48] tables. We ignore the higher-energy nonmolecular structures of nitrogen such as cg-N [84], considering only solid N2 crystals, where the molecules are bound by their mutual van der Waals attraction [76]. Since LDA and PBE do not explicitly include long-range van der Waals forces, we might expect some difficulty in describing the ground state.

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All N2 structures are essentially degenerate, differing by no more than 0.03 eV per atom as we go from αN2 to eN2. Thus current versions of DFT and electronic-structure algorithms, even including van der Waals interactions, cannot accurately determine the ground state of N2. We will study this in more depth in a future paper, but for now we will simply note that DFT calculations for pure nitrogen, and presumably for nitrogen-rich compounds, differ considerably depending on the choice of functional. One consequence of this is that the minimum entropy for this system ranges from −0.35 to −0.75 eV/atom, depending on the choice of functional.

Tungsten is naturally found in two forms [41], α–W (#106), the ground-state body-centered-cubic structure, and β–W (#107), commonly referred to by its Strukturbericht [43] designation A15. For this calculation we also considered
FIG. 2. (Color online) The relative enthalpy \( \Delta H \) of \( N_{1-x}W_x \) for the 108 structures listed in the Supplemental Material [48] plotted versus increasing tungsten concentration. These points were calculated using the Perdew-Burke-Ernzerhof (PBE) functional with VASP. Note that the enthalpy of structure #7 is above the upper limit of the graph. The meaning of the symbols is described in the caption to Fig. 1.

The face-centered-cubic structure (#108). Table II shows the equilibrium lattice constants for tungsten as a function of structure and density functional, as well as the energy difference predicted between the ground-state bcc structure and the other two structures. As usual, LDA underestimates the equilibrium lattice constant, while PBE overestimates it, and

FIG. 3. (Color online) The relative enthalpy \( \Delta H \) of \( N_{1-x}W_x \) for the 108 structures listed in the Supplemental Material [48] plotted versus increasing tungsten concentration. These points were calculated using the van der Waals vdW–DF2 functional with VASP. The meaning of the symbols is described in the caption to Fig. 1.
TABLE I. Equilibrium lattice constant, internal parameter, and equilibrium bulk modulus for the $Pb\bar{3}a$ structure (#1) of $\alpha$N$_x$, as determined using various density functionals and compared to experiment [45,85]. The lattice is simple cubic, and the nitrogen atoms sit on the (8c) Wyckoff position, which has one internal parameter $x$. The equilibrium lattice constant and bulk modulus are determined from a fourth-order Birch fit. The quantity $d$(N-N) is the length of the nitrogen-nitrogen bond in N$_2$ molecules.

<table>
<thead>
<tr>
<th>Functional</th>
<th>LDA</th>
<th>PBE</th>
<th>vdW–DF2</th>
<th>Expt. [45]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>5.223</td>
<td>6.187</td>
<td>5.511</td>
<td>5.659</td>
</tr>
<tr>
<td>$x$</td>
<td>0.061</td>
<td>0.052</td>
<td>0.058</td>
<td>0.056</td>
</tr>
<tr>
<td>$d$(N-N) (Å)</td>
<td>1.10</td>
<td>1.11</td>
<td>1.11</td>
<td>1.10</td>
</tr>
<tr>
<td>$K_0$ (GPa)</td>
<td>5.70</td>
<td>0.788</td>
<td>4.69</td>
<td>1.2 [85]</td>
</tr>
</tbody>
</table>

the vdW–DF2 lattice constant is even larger. All functionals give approximately the same energy difference between the three structures, indicating that the van der Waals contribution to the energy is, as one would expect, negligible for pure tungsten.

B. $\beta$-phase structures

The $\beta$-phase structures [14] (including the $\gamma$-NW phase described by Kiessling and co-workers [17–19]) can be described as tungsten nitride in the NaCl structure with vacancies on selected nitrogen and/or tungsten sites. In the extreme limits, this leads to the NaCl structure (#67 in the Supplemental Material [48]), with no vacancies, and a face-centered-cubic structure of tungsten (#108), with all nitrogen sites empty. Experiments [14–19,21,23] generally assume that the tungsten sites in $\beta$ (and $\gamma$) N-W are fully occupied, and that changes in stoichiometry are controlled by vacancies on the nitrogen sites, with possible tetrahedral nitrogen interstitials for the nitrogen-rich phases. As we will see in the following, density functional calculations do not support this point of view.

The lowest-energy $\beta$-phase structure, independent of the choice of functional, is NbO (#53) [68], a simple cubic supercell of NaCl with vacancies at the corners and in the center of the cube, as shown in Fig. 4. In itself this should not be particularly surprising, as NW and NbO have the same number of electrons in the valence band. However, no experimental papers claim discovery of the NbO structure. The closest structure to NbO was described by Kiessling and Peterson [16] as a structure with space group $Pm\bar{3}m$ with metal atoms on the (3c) Wyckoff sites. Instead of nitrogen occupying the (3d) Wyckoff sites, as would be found in NbO, they found both oxygen and nitrogen on the (1b)[1/2 1/2 1/2] and (3d) sites, equivalent to the $S_2$U$_4$ structure [65]. WYL+ [21] described a structure which they call "c-W$_3$N$_4$" ($x = 0.429$) containing no oxygen, which also takes on the $S_1$U$_4$ structure. While we did examine this structure (#47), we did not find it particularly close to the ground-state hull using any functional, although it does have a lower value of $\Delta H$ than the NaCl structure.

The NbO structure for tungsten nitride was recently examined by Liu, Zhou, Gall, and Khare [67], who computed its equilibrium lattice constants and elastic constants. They did not, however, compare its stability to the NaCl structure, nor find its place in the overall tungsten nitride phase diagram.

Our results show that many low-energy $\beta$-type structures in the N-W system can be constructed starting with supercells of the NaCl structure and removing selected N and W atoms. The general rule we found is that the resulting structure will have lower energy than NaCl if the resulting vacancies are not nearest neighbors (separation $a/\sqrt{2}$ for like atoms, $a/2$ for unlike atoms). This includes structures with large atomic relaxations, e.g., the Mo$_2$N structures [90] (#19 and #92), and structures which only allow relaxation of the lattice constant, e.g., $S_3$U$_4$ (#47 or #78) and the ground-state NbO structure.

The elastic constants of the NbO phase are given in Table III, along with the results of Liu et al. [67]. Each functional predicts this structure to be quite stiff, with bulk moduli about 30% smaller than diamond while the shear modulus is about 60% of diamond. This is somewhat stiffer than the moduli predicted by Aydin et al. [30] for their ReP$_4$ structure, and nearly as stiff as the $N_2$W structures predicted by Wang et al. [26]. While this is no guarantee that the structure is in fact hard, it does indicate that the NbO structure of tungsten nitride is a candidate for a superhard material. Unlike the $N_2$W and $N_4$W candidate structures mentioned elsewhere, every...
TABLE III. Equilibrium lattice and elastic constants of tungsten nitride in the NbO structure [space group Pm\(\overline{3}m\) #221, Wyckoff positions (3c) and (3d), #53 in the Supplemental Material [48]]. These were computed by VASP using the appropriate PAW potentials for each exchange-correlation functional. Elastic constants (in GPa) were computed by finite strain [80,81]. The isotropic shear modulus \(G\) is the average of the Hashin-Shtrikman bounds for a cubic system [88,89]. Starred results are from the paper of Liu, Zhou, Gall, and Khare [67].

<table>
<thead>
<tr>
<th>Functional</th>
<th>(a) (Å)</th>
<th>(C_{11})</th>
<th>(C_{12})</th>
<th>(C_{44})</th>
<th>(B)</th>
<th>(G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td>4.078</td>
<td>884</td>
<td>140</td>
<td>177</td>
<td>388</td>
<td>239</td>
</tr>
<tr>
<td>PBE</td>
<td>4.131</td>
<td>754</td>
<td>126</td>
<td>173</td>
<td>335</td>
<td>220</td>
</tr>
<tr>
<td>vdw–DF2</td>
<td>4.208</td>
<td>655</td>
<td>120</td>
<td>154</td>
<td>298</td>
<td>192</td>
</tr>
<tr>
<td>LDA*</td>
<td>4.063</td>
<td>903</td>
<td>131</td>
<td>174</td>
<td>388</td>
<td>240</td>
</tr>
<tr>
<td>PBE*</td>
<td>4.120</td>
<td>813</td>
<td>115</td>
<td>171</td>
<td>348</td>
<td>227</td>
</tr>
</tbody>
</table>

Functional predicts the NbO structure to be the ground-state structure at this composition.

In addition to the elastic constants shown in Table III, we further checked the stability of the NbO structure by computing the phonon spectra, as shown in Fig. 5. There are no imaginary frequency modes, indicating that the structure is stable.

The electronic band structure and density of states of the NbO phase are shown in Figs. 6 and 7, respectively. As in all cases in this paper, the high-symmetry \(k\) points are labeled following as in Lax [91] and by AFLOW [92]. The structure is a metal, with most of the electrons at the Fermi level being provided by the tungsten \(d\) states.

The change in enthalpy \(\Delta H\) for each of our \(\beta\)-phase structures is shown in Fig. 8. This is a subset of Fig. 2 containing only \(\beta\)-phase structures. Each point is color coded to show the concentration of vacancy sites on the underlying NaCl lattice, e.g., the NbO structure (#53) is a supercell of the NaCl structure with 25% of its sites vacant. We see that the lower-energy structures, particularly in the region of 50% tungsten, are dominated by unit cells with 25% or fewer vacancies. This suggests that the experimentally observed \(\beta\)-NW structures have the atoms arranged in a sodium chloride structure where each site is approximately 75% occupied, the exact vacancy fraction for each site depending on the composition. This picture fits with the experimental lattice constant [22] for the the \(\beta\) phase, which at 4.12–4.14 Å is similar to the lattice constants we obtain for the NbO structure (4.08 Å LDA, 4.13 Å PBE), and far below the lattice constant we obtain for the fully occupied NaCl structure (4.30 and 4.37 Å, respectively).

Contrary to published results [14–16,18,19,23], we see no evidence of stable \(\beta\)-phase NW\(_2\) structures, nor of any structures where all of the tungsten sites are occupied. For \(x\)

![FIG. 5. (Color online) Phonon frequencies along high-symmetry lines for the NbO structure (#53) of tungsten nitride, found with the MedeA® package [79]. No imaginary phonon frequencies were found, indicating that this structure is stable against small amplitude vibrations. The high-symmetry points and lines are described in the Supplemental Material [48].](image)

![FIG. 6. (Color online) The electronic band structure of tungsten nitride in the NbO structure (#53) at the PBE equilibrium (\(a = 4.131\) Å). The high-symmetry points and lines are described in the Supplemental Material [48].](image)

![FIG. 7. (Color online) The electronic density of states and angular momentum decomposed density of states for tungsten nitride in the NbO structure (#53). These were computed via the tetrahedron method in VASP. The primary contributions are from the N-\(p\) and W-\(d\) states, with the W-\(d\) states dominating the conduction band.](image)
tungsten nitride structure. Vacancies in supercells of the sodium chloride structure, described by various patterns of both nitrogen and tungsten on the tungsten sublattices. Experiments [18,19,21] suggesting that vacancies appear only in tungsten carbide and nickel arsenide, with alternating triangular sheets of nitrogen and tungsten atoms, stacked in hexagonal or rhombohedral phases consist of alternating layers of tungsten and nitrogen, with the stacking pattern ABABACABABCBC. Alternating planes of tungsten have an occupation factor of $\frac{2}{3}$, i.e., two-thirds of the tungsten sites are vacant, giving the $N_3W_2$ stoichiometry. Interestingly, WYL+ also considered a structure which they called “h-W$_2$N$_3$” ($x = 0.6$, #80); this structure is identical to the parent (i.e., no tungsten vacancies) $\delta^H_H$ structure of Khitrova and Pinsker (#80), except that placement of the tungsten and nitrogen atoms is reversed.

As we saw with the $\beta$-phase structures, atomistic calculations cannot readily model randomly placed vacancies. We approximated the random structures by creating supercells of the parent structures, and then removing various patterns of tungsten atoms to match the required stoichiometry. We also looked at structures slightly off the target stoichiometry. The Supplemental Material [48] describes the low-lying (within 0.2–0.3 meV/atom of the convex hull) structures we found by this method. It is necessarily incomplete, but we believe we have found structures extremely close to the actual minimum-energy structures.

Figure 9 shows some of the low-energy structures in this system, as a function of tungsten concentration (along the $x$ axis) and vacancy concentration (shading). We started by fully occupying all the tungsten sites in the six $\delta$ phases described by Khitrova and Pinsker [18,19], the “r-W$_2$N$_3$” phase found by WYL+ [21] (the circled structures in the diagram), and the WC structure (pentagons) proposed by Schönberg [49]. We then systematically removed atoms from the appropriate tungsten layers. In most cases, this lowered $\Delta H$, and two

C. $\delta$-phase structures

While the $\beta$ (and $\gamma$) phases in the N-W system can all be described by various patterns of both nitrogen and tungsten vacancies in supercells of the sodium chloride structure, $\delta$ phases consist of alternating triangular sheets of nitrogen and tungsten atoms, stacked in hexagonal or rhombohedral patterns, as in tungsten carbide and nickel arsenide, with experiments [18,19,21] suggesting that vacancies appear only on the tungsten sublattices.

Schönberg [49] suggested that the parent $\delta$ phase is the tungsten carbide structure (#61 in the Supplemental Material [48]), with vacancies on the tungsten sites. He did not pursue this idea, as at the time the determination of nitrogen positions in a tungsten nitride compound was impossible.

The first large-scale investigation of $\delta$ phases was done by Khitrova and Pinsker [18]. They found six $\delta$-phase structures, ranging in composition from $N_2W$ ($\delta^V_V$ structure #25 in the Supplemental Material [48]) to $NW_2$ ($\delta^H_H$, #101). While these end points do not have any vacancies, the intermediate structures ($\delta^H_H$, $\delta^H_H$, $\delta^V_V$, $\delta^V_V$) have vacancies on some tungsten planes.

Recently, WYL+ [21] found experimental evidence for a $\delta$-type rhombohedral structure which they designated “r-W$_2$N$_3$” ($x = 0.4$). This structure consists of close-packed planes of alternating layers of tungsten and nitrogen, with the stacking pattern ABABCACABABCBC. Alternating planes of tungsten have an occupation factor of $\frac{1}{2}$, i.e., two-thirds of the tungsten sites are vacant, giving the $N_3W_2$ stoichiometry.

FIG. 8. (Color online) A section of Fig. 2 showing only structures created by removing atoms from supercells of the NaCl structure. Yellow circles denote structures where 25% of the sites on the NaCl lattice are empty. Downward-pointing triangles have fewer than 25% of the sites vacant, and the redder triangles have fewer vacancies, culminating in the NaCl structure (#67). Upward-pointing triangles have more than 25% of the sites vacant, and are bluer as more sites become vacant. Known experimental structures are labeled by their prototype name.
of our derivative “r-W₂N₃” structures (#35 and #36) have the lowest ΔH of all structures in this study, independent of choice of functional. In addition, the two structures (which are numerically degenerate in energy) form part of the convex hull for the N-W system. The “h-W₂N₃” phase mentioned above is approximately 0.35 eV/atom above the ground-state phase, so it is at best a metastable state.

Of the two ground-state structures, #35 has a smaller unit cell than #36, so we will concentrate on it. Figure 10 shows the atomic positions for this structure. Its elastic constants, listed in Table IV, were computed using the finite displacement method contained in VASP, and were used to calculate the Reuss (lower) and Voigt (upper) bounds on the isotropic polycrystalline bulk and shear moduli [55]. The shear modulus is less than 200 GPa, so we cannot regard this as a candidate for a superhard structure.

The electronic band structure is shown in Fig. 11, and the electronic density of states in Fig. 12. There is a small density of states at the Fermi level, so this structure is a semimetal. We only show the results for the PBE calculation, but this behavior persists across all three choices of DFT. Similar behavior occurs in the nearly degenerate structure #36. Another low-energy δ-type structure is the hP₃ N₂W structure proposed by WLLX+ [26], which can be constructed by doubling the tungsten carbide (#61) unit cell in the z direction and removing one of the tungsten atoms. This structure is composed of N₂ dimers alternating with layers of tungsten, and so we will discuss it in the next section, although we do include it in Fig. 9.

In addition to the structures described above, we also looked at the structure labeled “h-W₂N₃” by WYL+ [21], which is the same as the δ₂N₂W₃ structure #80 with N and W occupations reversed, forming structure #43. The αSm structure [93], structures #25 and #91, consists of alternating close-packed layers (stacking NNW or NWW), and so can also be considered a δ phase. Finally, we tried modeling δ-like structures starting with N-W in the NaCl structure, considering it as a close-packed system with stacking ABCABCABC, removing two-thirds of the atoms in alternating tungsten layers, forming structure #38. While these structures had ΔH < 0, they were not near the convex hull using any functional.

D. N₂ phases

For our purposes, an N₂ phase is one in which we can readily identify nitrogen dimers inside a tungsten matrix. Aydın, Çiftci, and Tatar (ACT) [30] studied N₂W in the ReP₃ structure [63] (Supplemental Material structure #7) They equilibrated the system using the LDA functional and found a negative value for ΔH, and also computed the elastic constants and an
FINDING THE STABLE STRUCTURES OF N1−xWx... PHYSICAL REVIEW B 91, 184110 (2015)

FIG. 10. (Color online) The PBE minimum-energy structure #35, space group Cm−C3x(#8). This is an approximation to the “r-W2N3” structure, and has the proper number of tungsten vacancies in the unit cell [21]. In the experimental “r-W2N3” structure, the tungsten sites in the z = 0 plane are randomly occupied and do not necessarily have the pattern shown here.

estimate of the hardness, stating that this material should be superhard.

In the form proposed by ACT, this structure is of type N2, with elongated nitrogen dimers in a tungsten matrix. It is extremely difficult to equilibrate. Starting from the structure which the authors graciously provided us, we found a minimum-energy structure (#7) close to theirs as shown in Fig. 1. Unfortunately, we found that ΔH > 0, suggesting a difference in end-point energies in Eq. (1) in our calculation compared to ACT. In addition, when we used the ACT structure

TABLE IV. Density functional dependent elastic constants of structure #35, space group Cm(#8), Pearson symbol mC20, shown in Fig. 10. This is an approximate version of the “r-W2N3” structure [21]. We also include the Reuss (lower) and Voigt (upper) bounds on the isotropic polycrystalline bulk and shear moduli for these systems [55]. All distances are in Å, while the moduli are in GPa. Unlisted elastic constants are zero by symmetry. Note that the Reuss bulk modulus Bg is the equilibrium bulk modulus of the crystal given by $K_0 = -V_0P'(V_0)$, where $V_0$ is the equilibrium volume of the crystal.

<table>
<thead>
<tr>
<th>Functional</th>
<th>LDA</th>
<th>PBE</th>
<th>vdW–DF2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameters</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>4.963</td>
<td>5.035</td>
<td>5.132</td>
</tr>
<tr>
<td>b (Å)</td>
<td>8.547</td>
<td>8.666</td>
<td>8.836</td>
</tr>
<tr>
<td>c (Å)</td>
<td>6.015</td>
<td>6.101</td>
<td>6.213</td>
</tr>
<tr>
<td>β (°)</td>
<td>56.732</td>
<td>56.784</td>
<td>56.823</td>
</tr>
<tr>
<td>Elastic constants (GPa)</td>
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<td></td>
<td></td>
</tr>
<tr>
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<td>611</td>
<td>555</td>
<td>484</td>
</tr>
<tr>
<td>C22</td>
<td>637</td>
<td>577</td>
<td>501</td>
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<tr>
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</tr>
<tr>
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<td>C15</td>
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<td>C35</td>
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</tr>
<tr>
<td>C46</td>
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<td>−6</td>
<td>−1</td>
</tr>
<tr>
<td>Bulk modulus (GPa)</td>
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</tr>
<tr>
<td>Reuss (Bg)</td>
<td>303</td>
<td>272</td>
<td>235</td>
</tr>
<tr>
<td>Voigt (Bv)</td>
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<td>274</td>
<td>237</td>
</tr>
<tr>
<td>Shear modulus (GPa)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Reuss (Gg)</td>
<td>194</td>
<td>177</td>
<td>117</td>
</tr>
<tr>
<td>Voigt (Gv)</td>
<td>197</td>
<td>180</td>
<td>137</td>
</tr>
</tbody>
</table>

FIG. 11. (Color online) The electronic band structure for structure #35, one of our approximations to the “r-W2N3” structure [21], using the PBE functional.

FIG. 12. (Color online) The electronic density of states for structure #35, one of our approximations to the “r-W2N3” structure [21], using the PBE functional and the tetrahedron method. Note that the angular momentum decomposed densities of states are summed over all atoms of the same type, even if they have different crystallographic positions.
with the PBE and vdW–DF2 functionals, we found ΔH to be large and positive, over 0.7 eV/atom in the PBE case.

Furthermore, with some manipulation of the structures we were able to obtain even lower-energy structures (#6). In the LDA case, we swapped the positions of the tungsten atoms with the second set of nitrogen atoms, and found an ΔH < 0 and much closer to the convex hull, though still not on it. This procedure did not lead to a low-energy structure for the PBE or vdW–DF2 functions, but when we expanded the volume of the LDA structure we found a double-well structure in the energy, where the higher volume had a lower energy. Backtracking from this, we found an even lower-energy structure at a volume comparable to the original LDA/ACT structure. When we used this minimized structure with the PBE and vdW–DF2 functionals, we obtained the structures designated (#6) in the Supplemental Material [48].

Given these results, we must conclude that the ACT structure is not the lowest-energy structure related to ReP4, that is, with space group Pbcn and all atoms on (8c) Wyckoff sites. In addition, all of the ReP4 structures are least 0.1 eV above the convex hull of the WN system, and so unlikely to be seen. However, we are not certain that we have found the minimum-energy structure within these constraints, for any choice of density functional, and we are continuing the search.

In addition to the ReP4 structure, we looked other candidates for the N2W ground state. The only low-energy structure we found was related to the metastable FeB4 structure proposed by Van der Geest and Kolmogorov [70]. We originally found the enthalpy of this structure to have ΔH ≈ 1 eV using the PBE functional. On transferring this structure from one computer to another we inadvertently transposed some atomic positions. The resulting structure, #8, is much lower in energy than the original converged structure, independent of the choice of functional, but it is still far from the convex hull. Given that we have found two structures with relatively low enthalpies, we cannot eliminate the possibility that a stable N2W compound exists, but at the moment this seems unlikely.

Compounds with stoichiometry N2W have been studied by other workers. WLLX+ [26] used an evolutionary method and found two nearly degenerate structures which we designate as #11 and #12. These are N2 dimers stacked in a hexagonal crystal alternating with tungsten atoms. The structures differ by the stacking patterns of the dimers, and they could be classified as either N2 phases or as β phases with missing tungsten planes.

Table V gives the equilibrium lattice constants and elastic constants of the two structures using all three density functionals. We compare our results to those of WLLX+, who looked at the systems using LDA and PBE. In all cases, both structures have relatively large bulk and shear moduli, and so are candidate superhard materials.

The structures #11 and #12 are the lowest-energy N2W systems within our LDA and PBE calculations. In the LDA they form part of the convex hull for the tungsten nitrogen system, as shown in Fig. 1.

### E. SiO2 phases

One of our approximate β-phase constructs, which we will designate c136 (#15 in the Supplemental Material [48]), had a surprisingly low enthalpy when we calculated its energy using the van der Waals vdW–DF2 functional. The c136 structure starts from a 32-atom body-centered-cubic supercell of the NaCl structure, with 4 nitrogen atoms and 10 tungsten atoms removed. This leaves only the (24h) and (12d) Wyckoff positions occupied, and so we originally classified it as a β-phase structure. However, as seen in Fig. 13 and described in Table VI, each tungsten atom is bonded to four nitrogen atoms arranged tetrahedrally, and each nitrogen atom is bound to two tungsten atoms. This arrangement is reminiscent of many SiO2 structures [69], although this particular structure has not been seen experimentally.

We also looked some of the simpler SiO2 structures, including the high-temperature phase of quartz [94] (#16 in the Supplemental Material [48]), cristobalite [95] (#14), and tridymite [96] (#13). The low-temperature forms of these
The stable structures of N\textsubscript{1−x}W\textsubscript{x} . . .

**TABLE VI.** The c\textsubscript{136} structure of N\textsubscript{2}W, constructed from a 32-atom body-centered-cubic supercell of the NaCl structure. The space group is \textit{Im}\textit{3m}-\textit{O}\textsubscript{H}\textsubscript{9} (#229), the nitrogen atoms occupy the (24\textit{h}) Wyckoff positions (0\textit{yy}), and the tungsten atoms occupy the (12\textit{d}) sites (01\textit{4}1\textit{2}). The first N-W-N angle is for atoms lying on the surface of the cube cell. The second case has one of the N atoms in the interior of the cube.

<table>
<thead>
<tr>
<th>Functional</th>
<th>LDA</th>
<th>PBE</th>
<th>vdW</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a (\text{Å}))</td>
<td>10.273</td>
<td>10.383</td>
<td>10.490</td>
</tr>
<tr>
<td>(y)</td>
<td>0.1454</td>
<td>0.1455</td>
<td>0.1455</td>
</tr>
<tr>
<td>N-W bond (Å)</td>
<td>1.840</td>
<td>1.860</td>
<td>1.879</td>
</tr>
</tbody>
</table>

Angles:

- W-N-W: 108.7°, 108.6°, 108.5°
- N-W-N (face): 108.7°, 108.6°, 108.5°
- N-W-N (interior): 109.9°, 110.0°

FIG. 13. (Color online) The SiO\textsubscript{2}-like c\textsubscript{136} structure (#15 in the Supplemental Material [48]) predicted as the ground state of N\textsubscript{2}W by the vdW–DF2 functional. The basic structure looks the same using LDA, PBE, and vdW–DF2 functionals. The exact dimensions are described in Table VI. Note that this is a body-centered-cubic lattice, so the center of the cube and the cube corners are equivalent sites. The inversion sites are at the centers of the eight-atom rings, not on the tungsten atoms.

FIG. 14. (Color online) The electronic band structure for the SiO\textsubscript{2}-like body-centered-cubic c\textsubscript{136} structure (#15) of N\textsubscript{2}W described in the text. Calculations were done using the vdW–DF2 functional, including van der Waals forces, within \textit{VASP}. The top valence band has a very small dispersion, dropping to \(-0.05\) eV below the top of the valence band at \(P\). The gap is 0.75 eV, and is direct at \(\Gamma\). The LDA and PBE calculations produce similar band structures.

We also looked at some distorted rutilelike structures, which have bonding similar to SiO\textsubscript{2}. These include bixbyite [97,98], structures #41 and #42; \(\beta\)NbO\textsubscript{2} [99], structure #17; and PbO\textsubscript{2} [100] structure #21, which has the same valence electron count at NbO\textsubscript{2}. These structures had energies comparable to the SiO\textsubscript{2} structures discussed above. In particular, the relaxed \(\beta\)NbO\textsubscript{2} structure is quite close to the convex hull when we used the vdW–DF2 functional. All of these structures are insulating. Since the cubic c\textsubscript{136} structure was the first of these we found, and has the highest-symmetry primitive cell, we did band-structure calculations for it, as shown in Fig. 14. There is a direct band gap of 0.75 eV using the vdW–DF2 functional. The band structure is unusual in that there is a very flat band (0.05 eV maximum dispersion) at the top of the valence band. As shown in the electronic density of states plot, Fig. 15, this narrow band has strong nitrogen 2\(p\) character.

We also computed the elastic constants for the c\textsubscript{136} structure. Not surprisingly, this very low-density system has small elastic constants, as shown in Table VII. We expect the other SiO\textsubscript{2} structures to have similar shear moduli.

Given the large density of states near the top of the occupied bands in this system, we looked for structural...
TABLE VII. Elastic constants for the c136 structure of N,W, computed using the LDA, PBE, and vdW–DF2 functionals. Elastic constants were computed by the finite strain method [80], allowing the atoms to relax at each strain while fixing the unit cell. Equilibrium structural parameters are taken from Table VI. B is the equilibrium bulk modulus, and all elastic constants are in GPa. The shear modulus G is an average of the Hashin-Shtrikman bounds [88,89].

<table>
<thead>
<tr>
<th>Functional</th>
<th>C$_{11}$</th>
<th>C$_{12}$</th>
<th>C$_{44}$</th>
<th>B</th>
<th>C$<em>{11} - C</em>{12}$</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td>119</td>
<td>77</td>
<td>13</td>
<td>91</td>
<td>42</td>
<td>15</td>
</tr>
<tr>
<td>PBE</td>
<td>112</td>
<td>72</td>
<td>13</td>
<td>85</td>
<td>41</td>
<td>16</td>
</tr>
<tr>
<td>vdW–DF2</td>
<td>104</td>
<td>65</td>
<td>12</td>
<td>78</td>
<td>39</td>
<td>14</td>
</tr>
</tbody>
</table>

instabilities, including imaginary phonon frequencies and a possible magnetic state. While we have not done a complete examination of the phonon spectrum, those $k$ points we sampled all have positive phonon frequencies, and imposing a spin polarization on the crystal raises its energy. We conclude that the structure is at least metastable.

While all of SiO$_2$ structures we examined always have $\Delta H < 0$, none of them form part of the convex hull when we use the PBE or LDA functionals. The appearance of these structures on and near the vdW–DF2 convex hull (Fig. 3) is most likely an artifact of the van der Waals density functional.

F. Miscellaneous structures

In this section, we describe several low-energy structures that appear in Figs. 1–3. Many of these structures have been studied by others, as outlined in Sec. II.

While we did calculations for a number of structures with composition NW$_2$, including $\beta$ and $\delta$ phases, the most interesting structures we found were NW$_2$ in the hexagonal MoS$_2$ structure [101] (#89) and the rhombohedral $\alpha$MoS$_2$ structure [102] (#80). In all cases, the hexagonal MoS$_2$ structure had the lowest enthalpy of any NW$_2$ structure we studied, and within the LDA it was nearly touching the tie line. This structure has not been seen nor previously predicted in the N-W system. We show the LDA equilibrium structure in Fig. 16. While exhibiting the layered character of the MoS$_2$ structures, it is not two dimensional. In fact, the distance between atoms in adjacent tungsten layers (2.81 Å) is smaller than the distance between tungsten atoms in the plane (2.84 Å).

This structure was only run because it was available in the AFLOW database. If it had not been present there, it would not have been tested since we had no indication either experimentally or theoretically that the N-W system would support close-packed tungsten planes. This demonstrates the power of the structural database in investigating new systems.

Since this structure has a similar form to the $\delta$ structures, we tried to lower its energy by placing vacancies on the tungsten sites (#85 in the Supplemental Material [48]) and by adding interplaner nitrogen or tungsten atoms (#75, #89). In no case were we able to get an enthalpy below the parent MoS$_2$ structure.

This structure is close to the convex hull in the LDA, and in the hopes of finding an instability leading to a lower-energy structure, we did a preliminary test for hardness by computing the elastic constants of the hexagonal MoS$_2$ phase, shown in Table VIII. It is not particularly hard, having a shear modulus on the order of 100 GPa. It is, however, elastically stable, as the elastic constants satisfy the Born criterion [39]. The structure is metallic, as can be seen from the band structure (Fig. 17) and electronic density of states (Fig. 18).

We looked at various structures with composition NW, including nickel arsenide (#59), studied by Kroll, Schröter, ...
and Peters [24], and the zinc-blende structure (#65), studied by WYL+ [21]. The nickel arsenide structure, which could be considered a δ phase, is a few tenths of an eV above the NbO structure. The zinc-blende structure, which WYL find to be very stiff, is over 0.5 eV above NbO and so is unlikely to form.

No N3W structures were found near the convex hull. The closest two were structures molybdite (Mo3 [103], #9) and P3Tc (#10) [56] Song and Wang [29] studied P3Tc within the LDA, and found to have reasonable large bulk (303 GPa) and shear (156 GPa) moduli. They also found that it had negative enthalpy (1), which we confirm. However, as shown in Fig. 1, this structure is well above the convex hull within the LDA. The PBE and vdW–DF2 results show that the P3Tc is positive. It is unlikely, therefore, that N3W exists in the P3Tc structure.

One-half of the nitrogen atoms in the relaxed molybdite structure (which looks nothing like molybdate) form N2 dimers with spacing 1.12–1.13 Å. The relaxed P3Tc structure is similar, with N2 dimers spaced 1.2 Å apart. We can therefore classify both structures as partial N2 phases.

Both structures have the same Pnma space group, with all atoms occupying (8c) Wyckoff positions, so it may be possible to transform from P3Tc to MoO3 by simply varying the c/a and b/a ratios. Such a transformation would reveal the structure of the energy barrier between the two states. Since these structures are well above the minimum-energy structure, we have not investigated this further.

V. DISCUSSION

To truly predict the structure of a compound AMBN, we must find the lowest-energy structure at that composition, but we must also determine if that structure is unstable with respect to decomposition into either into its end points or to some intermediate structures. When doing approximate density functional theory calculations, we should also be sure that the predicted structure is stable or metastable with respect to different functionals since current functionals are only approximations to the real one.

Using the tungsten nitride system as an example, the AFLOW high-throughput method was used to calculate the relative enthalpy (1) of over 500 structures at variety of compositions N1−xWx. We then studied over 100 of these structures in detail, using the generalized-gradient PBE functional, the local density approximation, and the van der Waals vdW–DF2 functional to produce a zero-temperature phase diagram over a wide variety of compositions.

For x > 0.4, all three functionals give the same predicted ground states: at x = 0.4, a hexagonal δ-NW structure with random vacancies on the tungsten sites, which we approximated using various supercells of the parent structure with different patterns of tungsten vacancies; and the β-NW structure, with the lowest state the ordered NbO structure, the sodium chloride structure with one-fourth of the sites vacant.

All three functionals show the importance of vacancies in the tungsten nitride system. If we consider the sodium chloride and tungsten carbide structures as the parents of the NW β and δ phases, we can nearly always lower the energy by constructing a supercell and removing selected atoms, as shown in Figs. 8 and 9. All of the 0 < x < 1 structures on the convex hull in Figs. 1–3 can be constructed by removing atoms from supercells of the parent structures. This is in agreement with experiment, which finds random vacancies in almost every structure.

What is not in agreement with experiment is the actual composition of the β phase. We find the lowest-energy structures near x = 7/5, while experiment tends to favor cubic structures with x ≈ 2/3. The likeliest explanation is in the kinetics of the tungsten-nitrogen reaction. It is very difficult to dissolve N2 molecules into tungsten [23], and so it is plausible that the energy barriers in the problem will favor tungsten-rich compounds. A thorough investigation of the kinetics of tungsten nitride formation is necessary for further understanding.

As noted, our original motivation for looking at the tungsten nitride system was the possibility of forming hard carbon-free materials. Previous calculations suggested that specific N2W and N4W structures were stable, had large bulk and shear
moduli (over 200 GPa), and were candidate hard structures. We found the N$_2$W compound [30] to be well above the convex hull, so that it would tend to phase separate into N$_2$ and either N$_2$W or N$_2$W$_2$, depending on the choice of density functional. The candidate N$_2$W structures [26] are on the LDA convex hull, but not the PBE or vdW–DF2 hulls, and so might be found at some future date. The experimentally observable “r-W$_2$N$_7$” structure has the lowest value of $\Delta H$ in the entire system. Unfortunately, it is not particularly hard, as our estimated shear modulus is under 200 GPa. However, the $\beta$-phase ground-state NbO structure does have shear moduli over 200 GPa, and so might be “hard.” This will require more investigation, similar to what Aydin, Ciftci, and Tatar [30] did for their N$_2$W candidate.

Another surprise coming out of this study is the change in the shape, depth, and composition of the convex hull depending on the choice of density functional. In the absence of spin-polarization effects, the DFT community usually thinks of the generalized-gradient approximation, and especially the PBE and related functionals, as improving on the LDA predictions of lattice constants, but not changing the ordering of structures. For $x \geq 0.4$, that is more or less true here. However, for nitrogen-rich systems there is considerable disagreement about the ordering of structures. This is most likely caused by the neglect of van der Waals forces in the nitrogen-rich systems. To test this, we used a common van der Waals functional, vdW–DF2. It indeed provides a better lattice constant for the solid N$_2$ but it also leads to what seems to be a spurious prediction of the ground-state structure at N$_2$W. It also consistently overestimates the lattice constants for systems with $x > \frac{1}{2}$, with equilibrium volumes even larger than the PBE predictions.

In summary, we have used high-throughput density functional calculations to map out the low-energy structures in the tungsten nitride system. In general, we find that previously proposed structures, both theoretical and experimental, are not the ground-state structures in this system, with the exception of the “r-W$_2$N$_7$” structure. We do find that $\beta$-phase structures can be described as various vacancy patterns on the sodium chloride structure, but we cannot explain the experimental preference for tungsten-rich $\beta$-phase structures. We also find that none of the density functionals we used correctly describe the system over all compositions, as the LDA and PBE neglect van der Waals forces and the vdW–DF2 functional produces what appear to be spurious predictions for equilibrium structures.

We have also shown that predictions of structural stability must include knowledge of structures over the entire range of compositions. Many of the studies described in Sec. II found structures with negative formation energy $\Delta H$ [Eq. (1)], but most of these are not on the convex hull of the tungsten nitride system. One of the structures that is close to the hull, MoS$_2$, would never have been studied if it were not in the database, as there was no indication that it was likely to occur. The high-throughput mechanism provided by AFLOW is therefore necessary to understand any compound system.

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[79] MedeA® is a registered trademark of Materials Design Inc.


[87] VASP includes a mode which determines the equilibrium structure by minimizing the pressure. However, pressure is not a variational quantity, and N₂ is a soft crystal, meaning that small errors in the pressure can produce large errors in the equilibrium volume. The error will indeed decrease with increasing numbers of plane waves, but it is much easier to determine the equilibrium configuration by direct calculation.


[95] P. Woodward, Structures based on linked polyhedra, [http://chemistry.osu.edu/~woodward/ch754/str_poly.htm](http://chemistry.osu.edu/~woodward/ch754/str_poly.htm)


As quoted in the American Mineralogist Crystal Structure Database, [http://rruff.geo.arizona.edu/AMS/amcsd.php](http://rruff.geo.arizona.edu/AMS/amcsd.php)


