4-10-2020

Indentation-Strain Stiffening in Tungsten Nitrides: Mechanisms and Implications

Cheng Lu

China University of Geosciences, lucheng@calypso.cn

Changfeng Chen

University of Nevada, Las Vegas, changfeng.chen@unlv.edu

Follow this and additional works at: https://digitalscholarship.unlv.edu/physastr_fac_articles

Part of the [Mineral Physics Commons](#)

Repository Citation

Lu, C., Chen, C. (2020). Indentation-Strain Stiffening in Tungsten Nitrides: Mechanisms and Implications. *Physical Review Materials*, 4(4), 1-11. American Physical Society.
<http://dx.doi.org/10.1103/PhysRevMaterials.4.043402>

This Article is protected by copyright and/or related rights. It has been brought to you by Digital Scholarship@UNLV with permission from the rights-holder(s). You are free to use this Article in any way that is permitted by the copyright and related rights legislation that applies to your use. For other uses you need to obtain permission from the rights-holder(s) directly, unless additional rights are indicated by a Creative Commons license in the record and/or on the work itself.

This Article has been accepted for inclusion in Physics & Astronomy Faculty Publications by an authorized administrator of Digital Scholarship@UNLV. For more information, please contact digitalscholarship@unlv.edu.

Indentation-strain stiffening in tungsten nitrides: Mechanisms and implications

Cheng Lu^{1,2,*} and Changfeng Chen^{2,†}

¹*School of Mathematics and Physics, China University of Geosciences (Wuhan), Wuhan 430074, China*

²*Department of Physics and Astronomy, University of Nevada, Las Vegas, Nevada 89154, USA*

(Received 12 February 2020; accepted 16 March 2020; published 10 April 2020)

We report on a systematic computational study of ideal strengths, i.e., the lowest stresses needed to destabilize a perfect crystal under a variety of loading conditions for six stable and metastable tungsten nitrides identified by advanced crystal structure search algorithms. We employ first-principles calculations to determine stress-strain relations and examine the corresponding atomistic bonding changes for a microscopic understanding of the structural deformation modes. The obtained results show that, in stark contrast to many previously studied transition-metal borides, carbides, and also most nitrides, the tungsten nitrides exhibit surprisingly broad and common patterns of strain-stiffening effects under indentation strains. These extraordinary behaviors are attributed to the favorable bonding arrangements in these materials, including the strong and well-connected W-W metallic bonds and $N \equiv N$ bonds in combination with W-N covalent bonds, which together create a strong three-dimensional bonding network that is capable of resisting large-indentation shear deformations, thereby greatly enhancing the corresponding mechanical strength that is directly responsible for the superior experimentally measured hardness results. These findings provide insights for elucidating unusual indentation strength enhancements in these materials and offer guidelines for exploring experimental synthesis and optimization of the presently identified and potentially additional very hard to superhard materials. These insights are also crucial for understanding the fundamental relationship between crystal and chemical bonding structures and the associated mechanical properties under a wide range of loading conditions in diverse application environments.

DOI: [10.1103/PhysRevMaterials.4.043402](https://doi.org/10.1103/PhysRevMaterials.4.043402)

I. INTRODUCTION

Transition-metal nitrides have attracted much attention in recent years due to their rich characteristics as high-temperature ceramics, superconductors, magnets, and catalysts, etc. [1–9]. Among these materials, tungsten nitrides represent a distinct family of compounds that exhibit high melting temperatures and desirable mechanical properties [10–12]. The electrical resistivity of tungsten nitrides is relatively low and it has a low tendency to react with other metals comparing with other transition-metal nitrides, indicating its suitability as a diffusion barrier [13]. Considerable efforts were made early on to synthesize tungsten nitrides in various stoichiometries. Hägg [14] first constructed the phase diagrams of W-N systems and reported the face-centered-cubic β phase, which has a chemical composition of W_2N . Kiessling and Liu [15] observed the γ phase of the W-N system, formed at about 825 °C–875 °C when tungsten metal was nitrized with ammonia. The γ phase is closely related to the β phase with a distorted face-centered lattice. Schönberg [16] later found the δ phase, which is isomorphous with WC, and confirmed the results of Hägg [14] in all respects, but could not verify the existence of the γ phase reported by Kiessling and Liu [15]. Recently, several additional tungsten nitrides, including hexagonal WN, hexagonal and rhombohedral W_2N_3 , and cubic W_3N_4 , were synthesized through a

solid-state reaction route under a moderate pressure of 5 GPa [17]. These compounds exhibit sensational elastic properties, which are on a par with those of cubic BN, suggesting that at least some of these tungsten nitrides are potentially superhard materials. A followup theoretical work established the convex hull of W_xN_y systems and determined low-energy structures in the W-N system [18]. However, despite numerous theoretical studies of tungsten nitrides covering the topics of structural stability, electronic and mechanical properties, and pressure-composition phase diagram [18–21], there is still a lack of understanding about the deformation modes and stress responses under indentation strain conditions that are most relevant to hardness testing. A systematic and in-depth study is therefore desirable to elucidate the atomistic mechanisms that determine key mechanical properties, especially indentation strengths that are directly related to hardness, for tungsten nitrides.

Recently, we carried out computational studies using first-principles calculations to examine stress-strain relations of selected tungsten nitrides under different deformation modes. Our results reveal surprisingly large indentation strain stiffening in two compounds, hP4-WN and hP6-WN₂, both of which adopt hexagonal crystal lattices [22]. The extraordinary strain-stiffening produces remarkably enhanced indentation strengths exceeding 40 GPa, placing these two compounds well above their peers among the large classes of transition-metal borides, carbides, and nitrides. Most importantly, hP4-WN is identified to be the first potential intrinsic superhard metal. This exciting finding raises questions on whether similar indentation strain-stiffening behaviors, which were rarely

*lucheng@calypso.cn

†chen@physics.unlv.edu

seen prior to our latest work [22], also exist in other tungsten nitrides. There have been extensive works in this area that have reported on the identification of various W-N structures that are viable at ambient conditions [17–21]. We have performed additional structure searches and the results are largely in agreement with previous reports. Six viable W-N structures are identified, including one cubic structure (cP6-WN) and five different forms of hexagonal structures (hP2-WN, hP4-WN, hP6-WN₂, hP20-W₂N₃, and hP22-W₅N₆). Some of these predicted structures have already been experimentally synthesized [17]. There may exist additional W-N structures, especially metastable ones, that are not included in this list, but these identified structures are sufficient for our current purpose of a relatively broad-based, although not necessarily exhaustive, examination of indentation strain stiffening effects among a diverse range of tungsten nitrides that host different crystal symmetries, chemical stoichiometries, and local bonding configurations. We have performed a systematic investigation of the stress-strain relations of these six tungsten nitrides as representative cases. The deformation processes associated with the mechanical failure modes under Vickers indentation loading conditions offer detailed information about the atomistic mechanisms which determine the strengths of these tungsten nitrides. Our calculations show that while hP4-WN and hP6-WN₂ may be placed into the superhard category, the remaining four W-N structures are unlikely to be intrinsically superhard. Nevertheless, these additional tungsten nitrides mostly exhibit indentation strain stiffening behaviors, which are attributed to the presence of the strong W-W metallic bonds and N $\equiv$ N bonds in combination with the W-N covalent bonds, which together create a strong three-dimensional network in the hexagonal crystal lattice that can resist large shear deformation under Vickers indentation loading.

In this paper, we present a comprehensive report on our computational findings on the stress responses under various strains, especially indentation shear compared with pure shear strains, in the six selected tungsten nitrides and discuss the underlying atomistic mechanisms responsible for their mechanical properties. We also discuss implications of the present results for designing and optimizing similar materials. In the next section, we describe computational methods and approaches that we employed in crystal structure searches as well as total-energy and stress-strain calculations. In Sec. III, we provide computational data, systematically detailing the stress-strain relations and the corresponding structural deformation modes for each of the six tungsten nitrides studied in this paper. In particular, we present in-depth analysis and discussion of the obtained results to elucidate the mechanisms and implications. We finally present a summary and main conclusions of the present paper in Sec. IV.

II. COMPUTATIONAL METHODS

While there are several existing works that explored the crystal structures of tungsten nitrides [17–21], the outcome is often sensitive to the specific search methods employed as well as computational details. We therefore have decided to perform a systematic crystal structure search to cross-check and compare with existing results. Our structural searches of W_xN_y are performed using the CALYPSO method [23,24],

which has been successfully applied to a large variety of materials [25–33]. The structural relaxations and total-energy calculations are performed by VASP code [34,35]. The generalized gradient approximation (GGA) and local density approximation (LDA) exchange and correlation functionals provided by VASP is adopted in the calculations. The electron-ion interactions are described by means of projector augmented wave method [35]. The 5d⁴6s² of W and 2s²2p³ of N atoms are treated as valence electrons, respectively. The enthalpy calculations are converged to 1 meV/atom with the cutoff energy of 700 eV, together with an adequately fine Monkhorst-Pack *k*-point sampling [36] in the Brillouin zone. The elastic constants are calculated based on the *ab initio* stress-strain method [37]. The phonon calculations are performed using the PHONOPY code [38]. The harmonic interatomic force constants are calculated by a large supercell, which is produced from the primitive cell and contains about 150 atoms. The supercell size and convergence tests are performed to obtain the accurate phonon dispersions. The computational details are shown in the Supplemental Material [39].

The energetic stability of W_xN_y stoichiometries are quantified by constructing the ground-state convex hull, which is built from the formation enthalpy per atom of the most stable structures at each stoichiometry: $\Delta H = [H(W_xN_y) - xH(W) - yH(N)]/(x+y)$, where ΔH is the relative formation enthalpy per atom, and $H(W_xN_y)$, $H(W)$, $H(N)$ are the enthalpies of W_xN_y, bcc-W, and α -N with the inclusion of van der Waals forces, respectively. Remarkably, the predictions for stable stoichiometric compositions are strongly dependent on the choice of exchange-correlation functionals. The GGA shows that cP6-WN and hP20-W₂N₃ are possible stoichiometries to be experimentally synthesized. By contrast, in the LDA case, hP20-W₂N₃, hP22-W₅N₆, and hP6-WN₂ are the three stable compounds in the tungsten nitrides. The detailed results are listed in Fig. S1 in the Supplemental Material [39].

First-principles calculations of stress responses to strains depict the material deformation and strength under different loading conditions including tensile and shear [40–50], and calculated indentation strengths are able to directly compare with the well-regulated nanoindentation measurements [51–53]. Under indentation deformation, shear unstability generally takes precedence over the cracks and dislocations [54], showing the initiation of plasticity [43,45], and bond break will appear under a compressive stress [55,56]. The indentation strength is calculated by an ideal indenter, containing a normal compressive (σ_{zz}) and a shear stress (σ_{zx}) component that satisfy the criterion $\sigma_{zz} = \sigma_{zx} \tan \phi$, where ϕ is the centerline-to-face angle of the indenter [55,56]. The pure shear deformation mode corresponds to $\phi = 0$. We have performed calculations for many material systems, including both traditional strong covalent materials and transition-metal light-element compounds, and the calculated indentation strengths well describe the experimentally load-invariant indentation hardness [47–49,57–70].

III. RESULTS AND DISCUSSION

Our calculations reproduce previously reported stable and metastable W-N structures [17–21] and also identify an additional stable hP20-W₂N₃ phase that possesses hexagonal

FIG. 1. Crystal structures of six tungsten nitrides examined in this paper: (a) cP6-WN, (b) hP2-WN, (c) hP4-WN, (d) hP20-W₂N₃, (e) hP22-W₅N₆, and (f) hP6-WN₂.

$P6_3/mcm$ symmetry and contain four W₂N₃ formula units per unit cell. It is 0.345 eV/atom lower in enthalpy than the experimentally assigned $P6_3/mmc$ phase [17]. The equilibrium lattice parameters of the hP20-W₂N₃ are $a = b = 5.0032$ Å, $c = 10.0889$ Å, with W at Wyckoff 6g (0.3425, 0.0000, 3/4), 2b (0.0, 0.0, 1/2), and N atoms at 12k (0.6752, 0.0, 0.6229) positions. Each tungsten atom forms a sixfold coordinated octahedron with nitrogen atoms arranged at the corners, while each nitrogen atom is surrounded by four tungsten atoms. The predicted stable and some higher-enthalpy metastable crystal structures may all be viable for synthesis [18]. This scenario is supported by the recent experimental work that produced metastable W-N structures [17]. For the present paper, we have selected the four predicted stable tungsten nitrides plus two metastable ones, hP2-WN and hP4-WN, which have been shown by previous work [17,18] and also our study [22] to be metastable and relevant to experimental synthesis.

The crystal structures of the six tungsten nitrides are shown in Fig. 1. We have determined their optimized structural parameters (Table I), elastic constants (Table II), and phonon dispersions (Fig. 2). The obtained results indicate that these compounds are all mechanically and dynamically stable, which combined with the energetic data indicate overall structural stability or metastability. Having determined the crystal structures, we follow the well-established procedures to assess indentation strengths by evaluating stress responses to indentation shear deformations [64–70]. In this section, we present and discuss the calculated indentation shear stress responses compared with pure shear results to probe and elucidate indentation strain stiffening phenomena in the selected tungsten nitrides. It is worth emphasizing that we do not attempt to conduct an exhaustive examination of stress responses in all shear planes, which is a practically unattainable task and, more pointedly, is unnecessary for the understanding of the issues at hand in the present paper, but instead we aim to investigate representative cases to identify indentation strain-stiffening effects and explain the underlying atomistic mechanisms. In particular, it is recognized that crystals tend to exhibit extremal strengths along high-symmetry low-index crystallographic directions [40–50], and these directions include those with weak tensile stresses that determine easy cleavage planes and the strong directions that exhibit contrasting behaviors. Below we focus on representative high-symmetry crystal planes for each tungsten nitride structure to explore the indentation strengthening effects.

A. Cubic cP6-WN

For cubic cP6-WN, we examine pure and indentation shear deformations in its (110) plane, which is equivalent to the (110) and (001) planes. In Figs. 3 and 4, we show the calculated stress responses to pure and indentation shear strains in the (110) plane along two perpendicular slip directions [001] and [110], respectively. At equilibrium ($\epsilon = 0$), each N

TABLE I. Calculated structural parameters for the six tungsten nitrides studied in this paper.

Structure	Symmetry	Lattice parameters	Atomic coordinates			
			Atom	x	y	z
cP6-WN	$Pm\bar{3}m$	$a = b = c = 4.1194$ Å $\alpha = \beta = \gamma = 90^\circ$	W(3d)	0.5000	0.0000	0.0000
			N(4g)	0.5000	0.5000	0.0000
hP2-WN	$P\bar{6}m2$	$a = b = 2.8632$ Å; $c = 2.9009$ Å $\alpha = \beta = 90^\circ$; $\gamma = 120^\circ$	W(1a)	0.0000	0.0000	0.0000
			N(1f)	0.6667	0.3333	0.5000
hP4-WN	$P6_3/mmc$	$a = b = 2.8504$ Å; $c = 5.7859$ Å $\alpha = \beta = 90^\circ$; $\gamma = 120^\circ$	W(2a)	0.0000	0.0000	0.0000
			N(2c)	0.3333	0.6667	0.2500
hP6-WN ₂	$P6_3/mmc$	$a = b = 2.9284$ Å; $c = 7.7885$ Å $\alpha = \beta = 90^\circ$; $\gamma = 120^\circ$	W(2d)	0.3333	0.6667	0.7500
			N(4e)	0.0000	0.0000	0.5901
hP20-W ₂ N ₃	$P6_3/mcm$	$a = b = 5.0031$ Å; $c = 10.0884$ Å $\alpha = \beta = 90^\circ$; $\gamma = 120^\circ$	W(6g)	0.3425	0.0000	0.7500
			W(2b)	0.0000	0.0000	0.5000
			N(12k)	0.6752	0.0000	0.6229
			W(2a)	0.0000	0.0000	1.2500
hP22-W ₅ N ₆	$P6_3/mcm$	$a = b = 4.8974$ Å; $c = 11.2623$ Å $\alpha = \beta = 90^\circ$; $\gamma = 120^\circ$	W(4c)	0.6667	0.3333	1.2500
			W(4d)	0.6667	0.3333	1.0000
			N(12k)	0.0000	0.3328	0.6303

TABLE II. Calculated elastic constants C_{ij} (in GPa) for the six tungsten nitrides studied in this paper. These elastic constants all satisfy the mechanical stability criteria for the corresponding crystals [71].

Phase	C_{11}	C_{33}	C_{44}	C_{66}	C_{12}	C_{13}
cP6-WN	843.28		174.89		124.28	
hP2-WN	656.56	714.83	100.21	228.95	198.66	277.82
hP4-WN	620.02	765.59	294.82	184.16	251.70	268.57
hP6-WN ₂	585.38	983.61	236.27	195.28	194.82	212.61
hP20-W ₂ N ₃	559.88	451.43	188.07	202.39	155.10	123.90
hP22-W ₅ N ₆	623.57	728.59	248.67	204.66	214.25	173.12

atom is coordinated with four W atoms with an equivalent W-N bond length of 2.060 Å. Under pure shear strains, the W-N covalent bonds are stretched to 2.200 Å at the peak shear strain of 0.435. In contrast, the distance between neighboring W atoms decreases from 2.913 Å to 2.531 Å, producing new W-W metallic bonds, as shown in Fig. 3. The W-N bonds form a strong network, and combined with the W-W metallic bonds they effectively resist pure shear deformation and produce a peak shear stress of 48.8 GPa. Past the peak strain of 0.435, all the W-W bonds and one of the W-N bonds in the network break, leading to a structural reconstruction. Meanwhile, under the $(1\bar{1}0)[001]$ indentation shear, cP6-WN undergoes a two-step structural failure with the stress first increasing monotonically to the peak value

FIG. 2. Calculated phonon dispersion relations of the six tungsten nitrides studied in this paper. There is no imaginary phonon mode in the entire Brillouin zone in any of the six cases, indicating dynamic stability of these structures.

FIG. 3. Calculated stress-strain relations and key structural snapshots of cubic cP6-WN in the $(1\bar{1}0)[001]$ direction, which is equivalent to the $(110)[001]$ direction.

of 21.8 GPa at $\epsilon = 0.185$, followed by a stress reduction to 16.7 GPa at $\epsilon = 0.190$. No bonds are broken in this process, but the N atoms gradually sink into the center of the cube, caused by the normal indentation stress component, resulting in considerable bending of the linear W-N covalent bonds and a reduced stress to 14.0 GPa at $\epsilon = 0.260$. At further increased strains, the structure fails and stress drops precipitously. There is a significant indentation induced strength reduction in this case.

The deformation process of cP6-WN along the $(1\bar{1}0)[110]$ shear path exhibits structural instabilities at smaller shear strains compared to those in the $(1\bar{1}0)[001]$ case. But the two cases share similar deformation mechanisms under pure shear by breaking the W-N covalent bonds. The main difference is that no W-W metallic bonds are formed and broken, and the pure shear strength of cP6-WN in the $(1\bar{1}0)[110]$ direction is slightly lower at 43.8 GPa. The deformation process of cP6-WN under indentation shear in the $(1\bar{1}0)[110]$ direction is almost the same as that under the pure shear, with the stress monotonically increasing to the peak value of 32.2 GPa at $\epsilon = 0.110$ (Fig. 4). After passing the peak stress, the structure fails by the breaking of the W-N covalent bonds. Here the indentation strength is higher than that under the $(1\bar{1}0)[001]$

FIG. 4. Calculated stress-strain relations and key structural snapshots of cubic cP6-WN in the $(1\bar{1}0)[110]$ direction, which is equivalent to the $(110)[1\bar{1}0]$ direction.

FIG. 5. Calculated stress-strain relations and key structural snapshots of cubic cP6-WN in the (001)[110] direction, which is equivalent to the (001)[$\bar{1}\bar{1}0$] direction.

shear, but the result still represents a sizable indentation strain softening.

We show in Fig. 5 the calculated stress-strain curves in the (001) plane, which is the easy cleavage plane of cP6-WN. The results indicate that both pure shear and indentation shear strengths increase monotonically to peak values with rising strains. The structural snapshots show a different deformation process of cP6-WN in the (001)[110] direction compared with those in the (1 $\bar{1}0$) plane discussed above. Here there exist W-W metallic bonds under both pure shear and indentation shear deformations. The lengths of the W-W metallic bond are 2.669 Å at $\epsilon = 0.375$ under pure shear and 2.571 Å at $\epsilon = 0.290$ under Vickers indentation shear. As pure shear strain increases to 0.375, the W-N covalent bonds are stretched from 2.060 Å to 2.251 Å, above which both the W-W metallic bonds and one of the W-N covalent bonds in the cross-type network break, leading to a sharp drop of shear stress. Under indentation shear strains, the stress increases monotonically to a peak value of 28.2 GPa at $\epsilon = 0.290$, followed by a structural failure with a sharp stress drop.

B. Hexagonal hP2-WN

We next turn to hexagonal hP2-WN. We first show in Fig. 6 calculated stress-strain curves in the (001)[1 $\bar{1}0$] direction under pure shear and Vickers shear strains. The obtained lowest

FIG. 6. Calculated stress-strain relations and key structural snapshots of hexagonal hP2-WN in the (001)[1 $\bar{1}0$] direction.

FIG. 7. Calculated stress-strain relations and key structural snapshots of hexagonal hP2-WN in the (1 $\bar{1}0$)[001] direction.

peak stresses are 10.3 GPa under pure shear and 7.9 GPa under Vickers shear. Under pure shear deformation, the stress increases quickly to a peak value of 6.7 GPa at $\epsilon = 0.095$, followed by a slight decrease to 2.3 GPa at $\epsilon = 0.170$. As shear strain further increases to 0.500, the local structure around each W atom is recovered from a five-coordinated WN₅ to the original six-coordinated WN₆ and the shear stress drops to 2.2 GPa. It is noted that indentation shear stress-strain relations exhibit a similar creeplike behavior with shear strain increasing and the stress-strain curves under pure shear and indentation shear deformations are almost coincide with each other until the ideal indentation strength drops. It can be seen from Fig. 6 that the indentation shear stress first increases to a peak value of 6.9 GPa at $\epsilon = 0.080$ and then decreases to 2.4 GPa at $\epsilon = 0.165$ with a W-N covalent bond in WN₆ octahedra broken. As the shear strain increases further, the stress starts to increase to the maximum of 7.9 GPa at $\epsilon = 0.340$, and eventually decreases to 1.7 GPa at $\epsilon = 0.360$. No bonds are broken in this process; instead the W-N covalent bonds in WN₅ rectangular pyramids stretch considerably.

Figure 7 displays the calculated stress-strain curves of hP2-WN in the (1 $\bar{1}0$)[001] direction under pure shear and indentation shear deformations. Under pure shear deformation, the stress increases rapidly to a peak stress of 6.4 GPa at $\epsilon = 0.095$; it then decreases to 2.2 GPa at $\epsilon = 0.165$. As shear strain ϵ increases to 0.405, the main load-bearing W-N bond is stretched from 3.190 Å to 3.360 Å while the other W-N bonds in WN₅ rectangular pyramids are reduced by about 0.03 Å, producing the peak stress response. Under indentation shear strains, the stress increases monotonically to a maximum of 9.2 GPa at $\epsilon = 0.110$ and then decreases to 2.7 GPa at $\epsilon = 0.195$. The main load-bearing W-N bond in WN₆ octahedra is stretched from 2.338 Å to 2.658 Å and broken past the peak stress. As the shear strain increases further, the reconstructed structure generates a gradually increasing stress response, peaking at 6.9 GPa at $\epsilon = 0.325$, followed by a decrease to -2.5 GPa at $\epsilon = 0.395$. The atomistic mechanisms for this second stress response process is different from that of the pure shear where no bonds are broken. Under the indentation shear, the normal compressive pressure beneath the indenter

FIG. 8. Calculated stress-strain relations and key structural snapshots of hexagonal hP2-WN in the $(\bar{1}10)[110]$ direction.

in the $[1\bar{1}0]$ direction squeezes a pair of W-N atoms, leading to the formation of a new W-N bond with a length of 2.424 Å, as shown in Fig. 7, which enforces the WN_5 rectangular pyramid and reconstructs a new WN_6 octahedron.

The stress-strain relations of hexagonal hP2-WN along another inequivalent shear direction of $(\bar{1}10)[110]$ in the $(\bar{1}10)$ plane under pure shear and indentation shear deformations show distinct and highly unusual structural deformation processes (Fig. 8). Here we find a peak shear strength of 30.3 GPa at the shear strain $\epsilon = 0.235$ under pure shear deformation. With further increasing shear strain, the main load-bearing W-N covalent bond is stretched from 2.311 Å to 3.026 Å and breaks, releasing the shear stress and leading to the failure of the original crystal structure. Under indentation shear deformation, the indentation shear stress rises sharply, reaching a very high value of 53.0 GPa at $\epsilon = 0.095$, which is a 71.9% strengthening over the peak stress of 30.3 GPa under the corresponding pure shear deformation. This abnormal enhancement of the indentation strength in hP2-WN along the $(\bar{1}10)[110]$ direction is attributed to a series of atomistic processes highlighted by the key bonding features that the local WN_6 octahedra in hP2-WN are corner sharing, and it combines with the W-W metallic bonds to create a strong three-dimensional network that is capable of resisting large shear deformation under Vickers indentation. It is noted that the W-W metallic bonds between the adjoining WN_6 octahedra are absent under pure shear, which explains the much lower peak pure shear stress. We examined stress responses along other shear directions and found a 34.1% strain stiffening in $(110)[001]$ direction, where the crystal goes through similar structural evolutions and bond changes; meanwhile, we found no strain stiffening in the $(110)[1\bar{1}0]$ and $(001)[110]$ directions.

C. Hexagonal hP4-WN

We now investigate the stress-strain relations of another hexagonal WN structure, hP4-WN, under pure shear and indentation shear deformations. This structure has been studied before in our recent work [22]. Calculations show strong indentation strain stiffening in the $(\bar{1}10)$ plane along two inequivalent shear directions of $(\bar{1}10)[001]$ and $(\bar{1}10)[110]$. The main mechanism for the indentation stiffening is the enhancement of the metallic W-W bonds in the (001) planes [22]. In the following, we examine the stress responses in two

FIG. 9. Calculated stress-strain relations and key structural snapshots of hexagonal hP4-WN in the $(110)[001]$ direction.

previously unexplored cleavage planes of hexagonal hP4-WN under pure shear and indentation shear deformations.

Figure 9 shows calculated stress-strain curves of hP4-WN in the $(110)[001]$ direction under pure shear and indentation shear deformations. Under pure shear deformation, the shear stress increases rapidly to a peak stress of 30.0 GPa at shear strain $\epsilon = 0.170$. As shear strain ϵ increases, the main load-bearing W-N bond is stretched from 2.521 Å at $\epsilon = 0.200$ to 3.560 Å at $\epsilon = 0.205$, leading to structural failure and stress release. Under indentation shear along the $(110)[001]$ direction, the situation is similar to that in $(\bar{1}10)$ plane, with a 1.0% strain stiffening and the presence of the W-W metallic bond, which enhances the structure resisting the indentation shear deformation. The indentation shear stress initially increases to a peak stress of 30.3 GPa at $\epsilon = 0.130$ and then slightly decreases to 28.8 GPa at 0.135 due to that the main W-W bond is stretched from 2.575 Å to 2.584 Å. As the shear strain increases further, the stress drops to 5.0 GPa at the strain of 0.140. The atomic deformation mechanism here is similar to that in the pure shear case, with one of the W-N bonds in the WN_6 octahedra broken.

Figure 10 shows calculated stress-strain curves of hP4-WN in the $(001)[110]$ direction under pure shear and indentation shear deformations. Under pure shear, the shear stress rapidly increases to a peak stress of 29.5 GPa at $\epsilon = 0.175$. After passing the peak stress, the shear stress decreases to 18.3 GPa at $\epsilon = 0.185$ with a key W-N bond in the WN_6 octahedra broken, stretched from 2.191 Å in the initial structure to 2.729 Å. Under the $(001)[110]$ indentation shear, the normal compressive pressure beneath the indenter in the $[001]$

FIG. 10. Calculated stress-strain relations and key structural snapshots of hexagonal hP4-WN in the $(001)[110]$ direction.

FIG. 11. Calculated stress-strain relations and key structural snapshots of hexagonal hP4-WN in the (001)[$\bar{1}\bar{1}0$] direction.

direction squeezes the structure, which causes the formation of W-W metallic bonds, with a length of about 2.665 Å at $\epsilon = 0.160$, along the [001] direction. The peak stress in the (001)[$\bar{1}\bar{1}0$] direction under Vickers shear deformation is 33.3 GPa, which represents a 12.9% strain stiffening. The atomistic deformation mechanism of hP4-WN in another inequivalent direction of (001)[$\bar{1}\bar{1}0$] under indentation shear deformations is similar to that in the (001)[$\bar{1}\bar{1}0$] direction (See Fig. 11). There is a significant (more than 15%) enhancement of the shear strength of hP4-WN in the (001)[$\bar{1}\bar{1}0$] direction under indentation shear deformation, which is due to the formation of the W-W metallic bonds together with the presence of the W-N covalent bonds, creating a strong three-dimensional network in hP4-WN.

D. Hexagonal hP6-WN₂

In this section, we describe calculated stress-strain curves for hP6-WN₂. The obtained values along all directions under pure shear deformation are higher than 40 GPa, except for that in the ($\bar{1}\bar{1}0$)[$\bar{1}\bar{1}0$] direction with a peak value of 30.7 GPa. This is due to that the strong N $\equiv$ N bonds combined with the W-N covalent bonds in WN₆ octahedra make hP6-WN₂ highly resistant to pure shear deformations. We present in Fig. 12 the calculated stress-strain curves of hP6-WN₂ under pure and Vickers shear deformations in the ($\bar{1}\bar{1}0$)[$\bar{1}\bar{1}0$] direction, where the lowest stress peak of 21.9 GPa under Vickers shear deformation is obtained. Under pure shear strains, the peak stress along the ($\bar{1}\bar{1}0$)[$\bar{1}\bar{1}0$] direction is 46.2 GPa at $\epsilon = 0.350$, then decreases to 3.7 GPa at $\epsilon = 0.365$ with the stretch of the N $\equiv$ N bond length from 1.388 Å to 1.409 Å.

FIG. 12. Calculated stress-strain relations and key structural snapshots of hexagonal hP6-WN₂ in the ($\bar{1}\bar{1}0$)[$\bar{1}\bar{1}0$] direction.

FIG. 13. Calculated stress-strain relations and key structural snapshots of hexagonal hP6-WN₂ in the ($\bar{1}\bar{1}0$)[001] direction.

The indentation shear stress-strain relations exhibit different behaviors with increasing shear strains. It is seen from Fig. 12 that the indentation shear stress first increases to a peak value of 21.9 GPa at $\epsilon = 0.200$ and then decreases to 2.4 GPa at $\epsilon = 0.345$. No breaking of N $\equiv$ N or W-N bonds occur, as indicated by the structural snapshots shown in Fig. 12, but there is clear expansion of the WN₆ octahedra in hP6-WN₂.

The situation of the stress response in the ($\bar{1}\bar{1}0$)[001] direction is similar to that in the ($\bar{1}\bar{1}0$)[$\bar{1}\bar{1}0$] direction. There is a 17.4% softening of the shear strength of hP6-WN₂. The peak stress reduces from 48.3 GPa under pure shear to 39.9 GPa under Vickers shear deformation, and the calculated stress-strain curves are shown in Fig. 13. Under pure shear deformation, the shear stress increases rapidly to a peak stress of 48.3 GPa at $\epsilon = 0.295$. After passing the peak stress, the shear stress decreases to 28.5 GPa at $\epsilon = 0.335$ with one of the W-N bonds in the WN₆ octahedra broken and the N $\equiv$ N bond undergone a rotation. The atomic deformation mechanisms of hP6-WN₂ in the ($\bar{1}\bar{1}0$)[001] direction under indentation shear deformations are similar to those under pure shear. Under the (001)[$\bar{1}\bar{1}0$] indentation shear, the shear stress increases to the peak value of 39.9 GPa at $\epsilon = 0.225$ and then slightly decreases to 35.6 GPa at $\epsilon = 0.270$. With a small further increase in shear strain (at $\epsilon = 0.275$), one of the W-N bond in the adjacent WN₆ octahedra is broken, accompanied by a rotation of the N $\equiv$ N covalent bonds, causing a drop of the indentation shear stress.

In addition to the ($\bar{1}\bar{1}0$) plane, we have also examined stress-strain curves in the (001) and ($\bar{1}\bar{1}0$) planes along different inequivalent shear slip directions. From the calculated results, we find that the indentation shear strengths are softened by 26.1% and 23.7% along the (001)[$\bar{1}\bar{1}0$] and (001)[$\bar{1}\bar{1}0$] directions, respectively. However, under Vickers shear deformations in the ($\bar{1}\bar{1}0$)[001] and ($\bar{1}\bar{1}0$)[$\bar{1}\bar{1}0$] directions, there is unusual stress response, especially in the ($\bar{1}\bar{1}0$)[$\bar{1}\bar{1}0$] direction with more than 120% indentation strength enhancement [22].

E. Hexagonal hP20-W₂N₃

Figure 14 shows the stress-strain curves of hP20-W₂N₃ under pure shear and indentation shear deformations in the ($\bar{1}\bar{1}0$)[001] direction. At equilibrium, each of the center W atoms is coordinated by six N atoms, and each N atom is surrounded by four W atoms with different W-N bond lengths ranging from 2.044 Å to 2.106 Å. Under pure shear

FIG. 14. Calculated stress-strain relations and key structural snapshots of hexagonal hP20-W₂N₃ in the (110)[001] direction.

deformations, as shear strain ϵ increases to 0.135, one of the W-N covalent bonds, changes from 2.044 Å to 2.144 Å. After the strain ϵ increases further to 0.145, we observe that the W-N covalent bond is stretched to 3.267 Å and broken, which releases the shear stress. Under indentation shear deformation in the (110)[001] direction, the stress-strain relations display characters similar to those under pure shear. The peak value of the indentation stress is 18.3 GPa at $\epsilon = 0.105$. After the strain increases to 0.110, we note that the W-N covalent bond at the top corner is broken, and the stress drop sharply.

In addition to the (110)[001] direction, we have examined another inequivalent direction (110)[1 $\bar{1}$ 0] in the (110) plane for hP20-W₂N₃ under pure shear and indentation shear deformations. The calculated stress-strain curves are shown in Fig. 15, and the results show an obvious strain stiffening, about 38.7%, along the (110)[1 $\bar{1}$ 0] direction. The peak stress increases from 34.4 GPa at $\epsilon = 0.260$ under pure shear to 47.7 GPa at $\epsilon = 0.145$ under Vickers shear deformation. This result is ascribed to that the W-W metallic bonds combined with the W-N covalent bonds in WN₆ octahedra to form a strong three-dimensional network resisting the large indentation shear deformation. The shear stress increases to the peak stress of 34.4 GPa at $\epsilon = 0.260$. After passing the peak stress, the shear strength decreases to 19.1 GPa at $\epsilon = 0.340$, and further drops at $\epsilon = 0.345$ with one of the W-N covalent bonds in the WN₆ octahedra broken. Under indentation shear deformation, the normal pressure beneath the indenter compresses the structure and leads to the formation of the W-W

FIG. 15. Calculated stress-strain relations and key structural snapshots of hexagonal hP20-W₂N₃ in the (110)[1 $\bar{1}$ 0] direction.

FIG. 16. Calculated stress-strain relations and key structural snapshots of hexagonal hP20-W₂N₃ in the (1 $\bar{1}$ 0)[001] direction.

metallic bonds. The indentation shear stress increases rapidly to a peak stress of 47.7 GPa at $\epsilon = 0.145$. After passing the peak stress, the shear strength drops to 9.0 GPa at $\epsilon = 0.150$.

Figure 16 shows the stress-strain curves and the structural snapshots before and after deformation of hP20-W₂N₃ under pure shear and indentation shear deformations in the (1 $\bar{1}$ 0)[001] direction. As pure shear strain ϵ increases to 0.130, corresponding to the peak stress of 22.3 GPa, the W-N covalent bonds change from 2.106 Å to three pairs of W-N covalent bonds with the bond lengths of 2.129 Å, 2.096 Å, and 2.088 Å, respectively. After the strain ϵ increases further to 0.135, we observe that the W-N covalent bond in the lower left corner is broken and releases the shear stress. The structural failure process of hP20-W₂N₃ under indentation shear deformation is the same as under pure shear. At $\epsilon = 0.110$ shear strain, the W-N covalent bond in the lower left corner is broken, causing significant drops of the stress.

Figure 17 shows the calculated stress-strain curves of hP20-W₂N₃ under pure shear and indentation shear deformations in the (1 $\bar{1}$ 0)[110] direction. The structural failure process of hP20-W₂N₃ sheared along the (1 $\bar{1}$ 0)[110] direction is the same as those along the (110)[001] direction with a 15.5% enhancement of the shear stress. Under pure shear deformation, as shear strain ϵ increases to 0.130, one of the W-N covalent bonds at the top corner is broken, leading to a sharp stress drop. Under indentation shear deformation in the (1 $\bar{1}$ 0)[110] direction, the stress-strain relations display a character different from that under pure shear. The peak value

FIG. 17. Calculated stress-strain relations and key structural snapshots of hexagonal hP20-W₂N₃ in the (1 $\bar{1}$ 0)[110] direction.

FIG. 18. Calculated stress-strain relations and key structural snapshots of hexagonal hP22-W₅N₆ in the (1 $\bar{1}$ 0)[001] direction.

of the indentation stress is 24.6 GPa at $\epsilon = 0.190$. After the strain increases to 0.290, we note that the W-N covalent bond at the top corner and part of the W-W metallic bonds are broken and the shear stress drops quickly.

F. Hexagonal hP22-W₅N₆

The calculated stress-strain curves of hP22-W₅N₆ under pure shear and indentation shear deformations in (110)[001] direction are displayed in Fig. 18. Again, like hP4-WN along (001)[1 $\bar{1}$ 0] and hP6-WN₂ along the (110)[001] directions, both the pure shear and indentation shear stresses of hP22-W₅N₆ increase continuously to the maximum at strain $\epsilon = 0.125$. Then, the stress decreases slightly before dropping quickly at about 0.150 strain (pure shear at $\epsilon = 0.150$, and indentation shear at $\epsilon = 0.155$). For hP22-W₅N₆ under pure shear deformation, the W-N covalent bonds break at $\epsilon = 0.160$ with the disintegration of the WN₆ octahedra, releasing the shear stress from 20.1 GPa to 0.4 GPa. In contrast, the WN₆ octahedra in hP22-W₅N₆ do not disintegrate, but just reconstruct under indentation shear deformation due to the normal compressive pressure beneath the indenter that compresses the structure without appreciably stretching the W-N covalent bonds. The critical peak stress of hP22-W₅N₆ under indentation shear deformation along the (1 $\bar{1}$ 0)[001] direction is 22.6 GPa at $\epsilon = 0.125$, which is slightly lower than that under pure shear deformation (23.3 GPa).

A similar WN₆ octahedra fracture under pure shear deformation is observed in hP22-W₅N₆ along the (1 $\bar{1}$ 0)[110] direction (see Fig. 19). The shear stress increases monotonically to a maximum of 42.8 GPa at $\epsilon = 0.295$ and follows after slight decrease to 25.0 GPa at $\epsilon = 0.370$. No bonds are broken. Then the stress drops to 3.7 GPa at $\epsilon = 0.375$ accompanied by the breaking of the W-N bonds in WN₆ octahedra. Meanwhile, P22-W₅N₆ deforms under indentation shear deformation, reaching the peak stress of 25.9 GPa at $\epsilon = 0.190$ strain. The W-N bonds in WN₆ octahedra do not break. As the critical strain of 0.190 is exceeded, the indentation shear stress decreases gradually to $\epsilon = 0.365$ with the stretching of the W-N covalent bonds in the local WN₆ octahedra, which releases the indentation shear stress to 3.6 GPa.

Figure 20 shows the calculated stress-strain curves of hP22-W₅N₆ under pure shear and indentation shear deforma-

FIG. 19. Calculated stress-strain relations and key structural snapshots of hexagonal hP22-W₅N₆ in the (1 $\bar{1}$ 0)[110] direction.

tions in the (110)[001] direction. Under pure shear deformation, the shear stress increases to a peak value of 20.7 GPa at $\epsilon = 0.100$, and then the stress decreases to 12.5 at $\epsilon = 0.125$. Under indentation shear deformation, we have found a 15.5% enhancement of the shear strength, which is due to the four W atoms adjoining to form a parallelogram, and this new structural unit combines with the WN₆ octahedra to effectively resist large shear deformation under the Vickers indentation shear. As shear strain increases to 0.130, one of the W-N covalent bonds in the middle WN₆ octahedra is broken, causing a large drop of stress.

There is a significant (more than 47%) enhancement of the shear strength of hP22-W₅N₆ in the (110)[1 $\bar{1}$ 0] direction. Under pure shear deformation, the maximum shear stress is 33.6 at $\epsilon = 0.255$. Meanwhile, the maximum shear stress under indentation shear deformation is 49.7 GPa at $\epsilon = 0.150$, which stems from the formation of the W-W metallic bonds with the bond length of about 2.400 Å. As the shear strain ϵ increases further, it drops to 4.3 GPa at $\epsilon = 0.155$. The W-N bonds in WN₆ octahedra break, and the structure fails, as shown in Fig. 21.

Most interestingly, the calculations show that cP6-WN, hP2-WN, hP4-WN, hP20-W₂N₃ and hP22-W₅N₆ are in metallic states at equilibrium and remain in metallic states under the Vickers indentation loadings up to the peak stress. By contrast, the calculated results show that hP6-WN₂ is in a semiconducting state at equilibrium but is driven into metallic

FIG. 20. Calculated stress-strain relations and key structural snapshots of hexagonal hP22-W₅N₆ in the (110)[001] direction.

FIG. 21. Calculated stress-strain relations and key structural snapshots of hexagonal hP22-W₅N₆ in the (110)[1 $\bar{1}$ 0] direction.

states by the Vickers indentation loadings near the peak stress. The electronic densities of states of the six tungsten nitrides at equilibrium and under Vickers indentation shear loadings at the indicated strains near the peak stress values along (1-10)[001] and (1-10)[110] shear directions corresponding to the stress-strain relations discussed above are shown in Figs. S2-S7 [39].

IV. CONCLUSIONS

We have carried out extensive first-principles calculations to establish a systematic understanding of the stress-strain relations of several stable or metastable crystal structures of tungsten nitrides under various loading conditions. The calculated results show some similarities shared by five hexagonal

tungsten nitrides. In particular, it is seen that their ideal indentation strengths under the Vickers indenter can obviously be higher than their pure shear strengths along a wide range of directions. This unusual strain stiffening is attributed to the formation of the W-W metallic bonds, which are promoted by the compressive pressure under the indenter, and these W-W bonds combine with the N $\equiv$ N bonds and W-N covalent bonds in WN₆ octahedra that already exist in the original crystal structure to create a strong three-dimensional network that is capable of resisting large shear deformation under Vickers shear deformations. The calculated results also reveal interesting differences between the hexagonal and cubic tungsten nitrides, most notably the behavior of considerable bond softening of cubic cP6-WN, which is due to the large vacancies in the center of the structure. Our systematic comparative study of stress responses under pure and indentation shear deformations shows that the mechanical strength of these compounds does not correlate with the nitrogen content but rather depends on the crystal symmetry and local chemical bonding configurations in the crystal lattice. These insights provide useful guidance for elucidating the superior mechanical properties of select tungsten nitrides and for exploring and designing additional transition-metal light-element compounds that may exhibit similar or even further improved properties.

ACKNOWLEDGMENTS

This work was supported in part by National Natural Science Foundation of China under Grants No. U1804121 and No. 11304167.

- [1] L. Chatelain, E. Louyriac, I. Douair, E. Lu, F. Tuna, A. J. Wooles, B. M. Gardner, L. Maron, and S. T. Liddle, *Nat. Commun.* **11**, 337 (2020).
- [2] W. Sun, C. J. Bartel, E. Arca, S. R. Bauers, B. Matthews, B. Orvañanos, B. Chen, M. F. Toney, L. T. Schelhas, W. Tumas, J. Tate, A. Zakutayev, S. Lany, A. M. Holder, and G. Ceder, *Nat. Mater.* **18**, 732 (2019).
- [3] J. Du, C. Alvarez-Lamsfus, E. P. Wildman, A. J. Wooles, L. Maron, and S. T. Liddle, *Nat. Commun.* **10**, 4203 (2019).
- [4] J. Deng, N. Liu, J. Guo, and X. Chen, *Phys. Rev. B* **99**, 184409 (2019).
- [5] K. R. Babu and G.-Y. Guo, *Phys. Rev. B* **99**, 104508 (2019).
- [6] D. F. Urban and C. Elsässer, *Phys. Rev. B* **96**, 104107 (2017).
- [7] C. Li and D. Broido, *Phys. Rev. B* **95**, 205203 (2017).
- [8] F. Rivadulla, M. Bañobre-López, C. X. Quintela, A. Piñeiro, V. Pardo, D. Baldomir, M. A. López-Quintela, J. Rivas, C. A. Ramos, H. Salva, J. S. Zhou, and J. B. Goodenough, *Nat. Mater.* **8**, 947 (2009).
- [9] J. C. Crowhurst, A. F. Goncharov, B. Sadigh, C. L. Evans, P. G. Morrall, J. L. Ferreira, and A. J. Nelson, *Science* **311**, 1275 (2006).
- [10] H. Yu, X. Yang, X. Xiao, M. Chen, Q. Zhang, L. Huang, J. Wu, T. Li, S. Chen, L. Song, L. Gu, B. Y. Xia, G. Feng, J. Li, and J. Zhou, *Adv. Mater.* **30**, 1805655 (2018).
- [11] H. Jin, H. Zhang, J. Chen, S. Mao, Z. Jiang, and Y. Wang, *J. Mater. Chem. A* **6**, 10967 (2018).
- [12] Y. Zhu, G. Chen, Y. Zhong, W. Zhou, and Z. Shao, *Adv. Sci.* **5**, 1700603 (2018).
- [13] S. Asgary, M. R. Hantehzadeh, and M. Ghoranneviss, *Phys. Met. Metallogr.* **118**, 1127 (2017).
- [14] G. Hägg, *Ztsch. Physik. Chem. B* **7**, 339 (1930).
- [15] R. Kiessling and Y. H. Liu, *JOM* **3**, 639 (1951).
- [16] N. Schönberg, *Acta Chem. Scand.* **8**, 204 (1954).
- [17] S. Wang, X. Yu, Z. Lin, R. Zhang, D. He, J. Qin, J. Zhu, J. Han, L. Wang, H. Mao, J. Zhang, and Y. Zhao, *Chem. Mater.* **24**, 3023 (2012).
- [18] M. J. Mehl, D. Finkenstadt, C. Dane, G. L. W. Hart, and S. Curtarolo, *Phys. Rev. B* **91**, 184110 (2015).
- [19] H. Wang, Q. Li, Y. Li, Y. Xu, T. Cui, A. R. Oganov, and Y. M. Ma, *Phys. Rev. B* **79**, 132109 (2009).
- [20] J. Q. Qin, X. Y. Zhang, Y. A. Xue, X. T. Li, M. Z. Ma, and R. P. Liu, *Comput. Mater. Sci.* **79**, 456 (2013).
- [21] Z. L. Zhao, K. Bao, D. F. Duan, F. B. Tian, Y. P. Huang, H. Y. Yu, Y. X. Liu, B. B. Liu, and T. Cui, *Phys. Chem. Chem. Phys.* **17**, 13397 (2015).
- [22] C. Lu, Q. Li, Y. M. Ma, and C. F. Chen, *Phys. Rev. Lett.* **119**, 115503 (2017).
- [23] Y. C. Wang, J. Lv, L. Zhu, and Y. M. Ma, *Phys. Rev. B* **82**, 094116 (2010).

- [24] Y. C. Wang, J. Lv, L. Zhu, and Y. M. Ma, *Comput. Phys. Commun.* **183**, 2063 (2012).
- [25] J. Lv, Y. C. Wang, L. Zhu, and Y. M. Ma, *Phys. Rev. Lett.* **106**, 015503 (2011).
- [26] L. Zhu, H. Wang, Y. C. Wang, J. Lv, Y. M. Ma, Q. Cui, Y. M. Ma, and G. T. Zou, *Phys. Rev. Lett.* **106**, 145501 (2011).
- [27] L. Zhu, H. Y. Liu, C. J. Pickard, G. T. Zou, and Y. M. Ma, *Nat. Chem.* **6**, 644 (2014).
- [28] D. Zhou, Q. Li, Y. Ma, Q. Cui, and C. F. Chen, *J. Phys. Chem. C* **117**, 5352 (2013).
- [29] Q. Li, D. Zhou, W. Zheng, Y. Ma, and C. F. Chen, *Phys. Rev. Lett.* **110**, 136403 (2013).
- [30] M. Zhang, H. Y. Liu, Q. Li, B. Gao, Y. C. Wang, H. D. Li, C. F. Chen, and Y. M. Ma, *Phys. Rev. Lett.* **114**, 015502 (2015).
- [31] D. Zhou, Q. Li, W. Zheng, Y. Ma, and C. F. Chen, *Phys. Chem. Chem. Phys.* **19**, 4560 (2017).
- [32] C. Lu and C. F. Chen, *J. Phys. Chem. Lett.* **9**, 2181 (2018).
- [33] C. Lu, M. Amsler, and C. F. Chen, *Phys. Rev. B* **98**, 054102 (2018).
- [34] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- [35] G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- [36] H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- [37] J. F. Nye, *Physical Properties of Crystals* (Clarendon Press, Oxford, 1985).
- [38] A. Togo, F. Oba, and I. Tanaka, *Phys. Rev. B* **78**, 134106 (2008).
- [39] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevMaterials.4.043402> for more details on the structural search, phonon dispersion relations, and electronic densities of states of W_xN_y .
- [40] R. H. Telling, C. J. Pickard, M. C. Payne, and J. E. Field, *Phys. Rev. Lett.* **84**, 5160 (2000).
- [41] H. Chacham and L. Kleinman, *Phys. Rev. Lett.* **85**, 4904 (2000).
- [42] S. H. Jhi, S. G. Louie, M. L. Cohen, and J. W. Morris, Jr., *Phys. Rev. Lett.* **87**, 075503 (2001).
- [43] S. Ogata, J. Li, and S. Yip, *Science* **298**, 807 (2002).
- [44] D. M. Clatterbuck, C. R. Krenn, M. L. Cohen, and J. W. Morris, Jr., *Phys. Rev. Lett.* **91**, 135501 (2003).
- [45] S. Ogata, J. Li, N. Hirotsaki, Y. Shibutani, and S. Yip, *Phys. Rev. B* **70**, 104104 (2004).
- [46] X. Blase, P. Gillet, A. San Miguel, and P. Mélinon, *Phys. Rev. Lett.* **92**, 215505 (2004).
- [47] Y. Zhang, H. Sun, and C. F. Chen, *Phys. Rev. Lett.* **93**, 195504 (2004).
- [48] Y. Zhang, H. Sun, and C. F. Chen, *Phys. Rev. Lett.* **94**, 145505 (2005).
- [49] Y. Zhang, H. Sun, and C. F. Chen, *Phys. Rev. B* **73**, 144115 (2006).
- [50] M. G. Fyta, I. N. Remediakis, P. C. Kelires, and D. A. Papaconstantopoulos, *Phys. Rev. Lett.* **96**, 185503 (2006).
- [51] C. R. Krenn, D. Roundy, Marvin L. Cohen, D. C. Chrzan, and J. W. Morris, Jr., *Phys. Rev. B* **65**, 134111 (2002).
- [52] M. I. Eremets, I. A. Trojan, P. Gwaze, J. Huth, R. Boehler, and V. D. Blank, *Appl. Phys. Lett.* **87**, 141902 (2005).
- [53] T. Li, J. W. Morris, Jr., N. Nagasako, S. Kuramoto, and D. C. Chrzan, *Phys. Rev. Lett.* **98**, 105503 (2007).
- [54] A. Gouldstone, H. J. Koh, K. Y. Zeng, A. E. Giannakopoulos, and S. Suresh, *Acta. Mater.* **48**, 2277 (2000).
- [55] Z. C. Pan, H. Sun, and C. F. Chen, *Phys. Rev. Lett.* **98**, 135505 (2007).
- [56] Z. Pan, H. Sun, Y. Zhang, and C. Chen, *Phys. Rev. Lett.* **102**, 055503 (2009).
- [57] Y. Zhang, H. Sun, and C. F. Chen, *Phys. Rev. B* **73**, 064109 (2006).
- [58] Y. Zhang, H. Sun, and C. F. Chen, *Phys. Rev. B* **76**, 144101 (2007).
- [59] Z. Pan, H. Sun, and C. F. Chen, *Phys. Rev. B* **79**, 104102 (2009).
- [60] W. Zhou, H. Sun, and C. F. Chen, *Phys. Rev. Lett.* **105**, 215503 (2010).
- [61] W. Zhou, Y. Zhang, H. Sun, and C. F. Chen, *Phys. Rev. B* **86**, 054118 (2012).
- [62] B. Li, H. Sun, and C. F. Chen, *Nat. Commun.* **5**, 4965 (2014).
- [63] B. Li, H. Sun, and C. F. Chen, *Phys. Rev. Lett.* **117**, 116103 (2016).
- [64] J. Yang, H. Sun, and C. F. Chen, *J. Am. Chem. Soc.* **130**, 7200 (2008).
- [65] C. Zang, H. Sun, and C. F. Chen, *Phys. Rev. B* **86**, 180101(R) (2012).
- [66] C. Zang, H. Sun, J. S. Tse, and C. F. Chen, *Phys. Rev. B* **86**, 014108 (2012).
- [67] B. Li, H. Sun, C. Zang, and C. F. Chen, *Phys. Rev. B* **87**, 174106 (2013).
- [68] B. Li, H. Sun, and C. F. Chen, *Phys. Rev. B* **90**, 014106 (2014).
- [69] H. Wu, H. Sun, and C. F. Chen, *Appl. Phys. Lett.* **105**, 211901 (2014).
- [70] Q. Li, D. Zhou, W. Zheng, Y. Ma, and C. F. Chen, *Phys. Rev. Lett.* **115**, 185502 (2015).
- [71] Z.-j. Wu, E.-j. Zhao, H.-p. Xiang, X.-f. Hao, X.-j. Liu, and J. Meng, *Phys. Rev. B* **76**, 054115 (2007).