Contents lists available at ScienceDirect

Materialia

journal homepage: www.elsevier.com/locate/mtla

Full Length Article

Prediction of super hardness in transition metal hexa-nitrides from density functional theory computations

S.R. Kandel^a, B.B. Dumre^a, D. Gall^b, S.V. Khare^{a,*}

^a Department of Physics and Astronomy, University of Toledo, Toledo, OH 43606, USA
^b Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, USA

ARTICLE INFO

Keywords: Density functional theory First-principles calculation Hardness

ABSTRACT

Despite several decades of work on enhancing the hardness of transition metal nitrides (TMNs) for hard coating applications, their experimentally measured Vickers hardness (H_V) has saturated around 30 GPa. We break this saturation point by demonstrating a 43%–100% higher hardness in hexagonal WN_6 , MoN_6 and TaN_6 with $H_V = 59$, 52, and 43 GPa, respectively. For all 29 TMNs, we report the mechanical and vibrational properties of nitrogen rich h-MN₆ compounds computed with density function-based theory. Only 8 h-MN₆ (VN_6 , MnN_6 , CoN_6 , ZnN_6 , MoN_6 , TaN_6 , WN_6 , and IrN_6) are both mechanically and dynamically stable. Structurally, h-WN₆ consists of armchair like hexagonal ring of covalently bonded nitrogen atoms which form short and strong bonds lead to a high hardness. Band structure and Bader charge analyses indicate that h-WN₆ is a wide gap semi-conductor and higher charge transfer from metal to nitrogen. In contrast, the softest hexa-nitride, h-ZnN₆ ($H_V = 7$ GPa) is metallic and has occupied anti-bonding states along with a lower charge transferred. Cubic polymorphs have lower hardness values of, for example, $H_V = 14$ GPa for c-WN₆. This is attributed to fewer N-N covalent bonds and a smaller charge transfer, illustrating the importance of both crystal structure and composition.

1. Introduction

Although diamond is the hardest known material hitherto, it has some limitations. For example, when diamond is utilized to cut ferrous metals such as steel, iron carbide is formed due to the chemical reaction [1,2]. For such situations, other hard materials are sought after. Transition metal nitrides (TMNs) are considered as an alternative. The nitrogen atoms inside TMNs can form short, strong, and highly directional covalent bonds causing high hardness [3,4]. Additionally, the transition metals, which have a high density of valence electrons, contribute to ultra-incompressibility of the material by resisting when squeezed [4]. Besides being hard and incompressible, TMNs have been studied by scientific community for its outstanding mechanical property (high hardness), chemical inertness, high melting point, high thermal conductivity, and varying electrical resistivity from metal to non metal [5-15]. These properties enable TMNs to become materials of sustained interest for hard coating as well as semiconductor industries [16-20]. Many experimentally synthesized TMNs have shown high hardness values, thereby establishing their potential applications in hard coatings [7,16,21-27].

In the search of super-hard material (Vickers hardness, (Hv > 40 GPa [28]), Kaner et al. [4] has highlighted that the search of super-hard material could be achieved either by forming the short covalent bond between lighter elements such as nitrogen or by using the elements with

high valence electron densities such as transition metals. In this connection, theoretical and computational methods such as first principles calculations have also been successfully used to investigate hardness of various materials [7,29-31]. Several studies have predicted the superhard materials using density function theory (DFT) and beyond methods [7,29-34]. Starting with the ideas presented by Kaner et al. [4,29,30], we also have predicted a super-hard tungsten (W) nitride in the stoichiometric ratio of 1:6 (WN_6) which falls in hexagonal crystal structure of space group $R\bar{3}m$ with hexagonal axes. In this study, we have utilized DFT to calculate and compare mechanical properties of all the 29 TMNs and discussed their stability. Also, we have tried to extract the answer to the high hardness observed in some TMNs through the study of their electronic behavior. We finally calculate and compare mechanical properties of cubic WN₆ (space group $Im\bar{3}m$ referred to as c-WN₆ hereafter) with h-WN₆ and show that not only stoichiometry, but crystal structure is also important in determining hardness of a material.

Our investigation on mechanically and vibrationally stable hexagonal and cubic phases of MN_6 exposed the clue that super hardness is a unique property of hexagonal phase. Crystal structure and the amount of larger charge transfered from metal to nitrogen which can form a stronger ionic bonding, along with the semi-conducting nature of a material have significant role in the enhancement of hardness. Our calculated mechanical properties include lattice constants, elastic constants,

* Corresponding author. *E-mail address:* sanjay.khare@utoledo.edu (S.V. Khare).

https://doi.org/10.1016/j.mtla.2022.101550 Received 23 April 2022; Accepted 22 August 2022 Available online 23 August 2022 2589-1529/© 2022 Acta Materialia Inc. Published by Elsevier B.V. All rights reserved.





Young's modulus, shear modulus, bulk modulus, Poisson's ratio, Pugh's ratio, and Vickers hardness. It also includes Debye temperature, formation energies and electronic properties. Only 8 h- MN_6 were found to be both vibrationally and mechanically stable. We also compared mechanical properties of super-hard compound with cubic structure of same stoichiometric ratio to get an insight of possible explanation of super-hardness seen in tungsten hexa-nitride. Out of 29 h- MN_6 , five of them have showed some magnetic properties.

2. Computational methods

All the calculations were done by using Vienna Ab initio Simulation Package (VASP) which performs calculations based on DFT [26,35– 44]. Perdew-Burke-Ernzerhof (PBE) functional within Generalized Gradient Approximation (GGA) were used with Projector Augmented Wave (PAW) method [35–38,45–48]. The VASP pseudopotentials with inner electrons were considered for all 29 transitions metals where available, whereas for nitrogen, N pseudopotential was considered [7,25,26,49– 51]. Kinetic energy cut-off for plane waves was set to 600 eV. The convergence criteria for electronic and ionic iterations were set to 10^{-5} eV and 0.01 eV/Å, respectively [25,50], along with Γ -centered k-mesh of spacing $2\pi \times 0.03 \forall^{-1}$ in the Brillouin zone [29,30]. The initial structure for h-MN₆ was obtained from the theoretical work of Xia et al. [29], whereas the initial structure for c-MN₆ was taken from Li et al. [30].

Atomic positions, cell shape, and cell volume were relaxed while optimizing the geometry of the crystal structures. During the relaxation process, the presence of magnetic properties in the TMNs was also gauged. After relaxation, formation energy per formula unit of MN_6 was calculated as [7,38,52]:

$$E_{form} = E(MN_6) - E(M) - 3E(N_2) \tag{1}$$

Here, $E(MN_6)$ is ground state energy of TMN, E(M) is ground state energy of transition metal, and $E(N_2)$ is ground state energy of nitrogen dimer in vacuo [53]. All ground state energies were obtained from full relaxation of relevant unit cells.

Next, we obtained the elastic constant tensor, by calculating the Hessian matrix, which is used for further calculation of other elastic properties of TMNs. During the calculation of Hessian matrix using finite differences, the limiting strain of 0.015 ∀ was utilized. We are unable to calculate the exact stress-strain curve for any of the h-MN₆ compounds due to the limits on computational resources. However, the exact stressstrain curve has been calculated by Xia et al. [29] for h-WN₆ as a sample where the shear stress of 48.6 GPa was the elastic limit with the strain of 0.12. This compares to our result of 59 GPa. The crystal symmetry of space group $R\bar{3}m$ with hexagonal axes of h-MN₆ entails five independent elastic constants, $(C_{11}, C_{12}, C_{13}, C_{33}, \text{ and } C_{44})$, whereas for cubic crystal system of c-WN₆ in space group $Im\bar{3}m$ necessiates three (C_{11} , C₁₂, and C₄₄) [7,29,30,54–56]. The Bulk modulus (B), and the shear modulus (G) can be calculated by using fundamental elastic constants as suggested by Voigt-Reuss-Hill approximation [56]. Pugh's ratio (k), Poisson's ratio (v), and Young's modulus (E) were also determined by using the values of *B* and *G* as discussed in reference [7]. Finally, the Vickers hardness (H_V) is calculated by using the equation suggested by Tian et al. [7,36–38,57–59], which is based on the macroscopic parameters, i.e., the bulk and shear moduli of materials. We have also calculated the Debye temperature (θ_D) of the compounds using B and G [7,25,52,58,60]. According to Deus and Schneider, Debye temperature (θ_D) for the given material can also be estimated as:

$$\theta_D = a H_V^{1/2} \rho^{-1/6} M^{-1/3} + b \tag{2}$$

where *a* and *b* are linear fitting constants [25,61].

The relationship between hardness and electronic-structure was investigated by calculating electronic Local Density Of States (LDOS), Projected Density Of States (PDOS), and band structure [20,29,36]. Further to study the phonon stability for these compounds, the phonon DOS was computed by using Phonopy code, based on Density Functional

Perturbation Theory (DPFT) [38,62]. The study of charge transfer from metal to nitrogen was done with the help of Bader charge analysis [63–66]. The Crystal Orbital Hamilton Population (COHP) was calculated with the help of Local-Orbital Basis Suite Towards Electric-structure Reconstruction (LOBSTER) package which helps in the study of chemical bonding between atoms [38,67–72].

3. Results and discussions

3.1. Structural, mechanical, and vibrational properties

The optimized crystal structure of h-MN₆ (space group: $R\bar{3}m$) with various interatomic distances is shown in Fig. 1a-c, where M atoms are occupying 3b and N atoms are occupying 18h Wyckoff positions. Fig. 1a, 1b and 1c show the crystal structure in a-b, a-c and b-c planes, respectively. Fig. 1a shows a single unit cell with hexagonal ring formed by N atoms around a central M atom. Fig. 1b and c show layered structures in $2 \times 2 \times 2$ supercells formed due to alternating M atoms and nitrogen rings. We have also reported various interatomic distances (Fig. 1a-c) in Table S1 that have been observed in h-MN₆. In all 29 h-MN₆, N-N distances in the hexagonal rings vary from 1.34 Å to 1.46 Å, except in CrN_6 where two alternating N-N distances of length 1.46 Å and 1.41 Å are observed. In addition to N-N distances, we have come up with 7 unique interatomic distances that can be crucial in understanding the structure of h-MN₆. In Fig. 1a, we observe that a central M atom is encompassed by a nitrogen ring. However, from Fig. 1b and c, we conclude that the central M atom is actually surrounded by four nitrogen rings, as the nitrogen rings do not lie in a single plane. We have found that there are two nitrogen rings that are nearer and equidistant from the central M atom and other two nitrogen rings are farther and equidistant from that same central M atom. Fig. 1a shows one of the nearer nitrogen rings as observed from a-b plane. In the nearer nitrogen rings, there are two alternating varying M-N distances. The shorter distance is dubbed "p" and the longer distance "q". Similarly, the other two farther nitrogen rings have only one N atom nearer to the central M atom (distance "r"). Likewise, in the layered structures (Fig. 1b and c), there are two unique intermetallic distances ("s" and "t" in b-c plane, and "u" and "v" in a-c plane) when observed from two different planes. In 14 h-MN₆, these four intermetallic distances are equal and the rest 15 h-MN₆ have varying values. This unique geometry is observed in all 29 h-MN₆, however, these unique distances do not offer any clue to the relationship with stability and hardness in the material. As discussed in Section 1, the N-N bonds form a short and strong bond that enhances hardness in a material. The iconic N rings in h-MN₆ provide directional bonding that further strengthens hardness in the stable materials. As the high hardness in h-WN₆ motivated this work, lets discuss its example of the N-N bond length in hexagonal ring, which is 1.46 Å and identical to the bond length of N_2 pair found in PtN_2 that is supposed to stabilize the crystal and improve its elastic moduli by forming the strong covalent bond between the N₂ pair [73,74]. A type of material having density of around 1900 kg/m³ and bond dissociation energy around 80-120 kJ/mol are called as high-energy-density (HEDM) materials [75]. Our calculated N-N bond length (1.46 Å) for h-WN₆ further suggests that the N atoms in rings are singly bonded with bond energy of around 167 kJ/mol [30] and it has mass density of 8885 kg/m³ indicating that h-WN₆ may be taken as a new HEDM. Table S1 also reports coordination number in $h-MN_6$, where we observe them in the numbers of 6, 10 or 12. In 3d-block, there is only one material with coordination number 12 (TiN₆) and one other with 10 (CrN₆), the rest are all 6. However, in 4d-block, there are two materials (MoN₆ and NbN₆) with coordination number 12 and in 5d-block, there are three materials (WN₆, TaN₆ and ReN₆) with coordination number 12. We can correlate this increase in the number of materials with a higher coordination number in higher d-block elements with their increase in size as more and more ligands are necessary to surround the central M atom.



Fig. 1. MN_6 in hexagonal structures with various interatomic distances ((a), (b) and (c)), and cubic structure (d), drawn with the help of Visualization for Electronic and Structural Analysis (VESTA) [95].

Table 1			
Lattice constants (a, c), formation energy (E_{form}) and elastic tensor (C _{ii}) for both	vibrationally and mechanically	stable h-MN ₆ .

Gr.	М	a (Å)	c (Å)	C ₁₁ (GPa)	C ₁₂ (GPa)	C ₁₃ (GPa)	C ₃₃ (GPa)	C ₄₄ (GPa)	E_{form} (eV)
5	v	5.26	7.67	464	173	132	254	84	3.28
7	Mn	5.13	7.31	582	157	130	319	126	4.67
9	Co	5.12	7.50	436	84	76	281	95	5.42
12	Zn	5.45	7.75	308	158	96	185	61	5.21
6	Mo	6.18	4.58	677, 551.4ª	99, 68.2 ^a	145, 114.1ª	736, 625.0 ^a	354, 312.2 ^a	7.60
5	Та	6.22	4.70	656	113	165	681	312	5.39
6	W	6.16, 5.69 ^b , 6.152 ^c	4.57, 4.23 ^b , 4.562 ^c	724, 662.1ª, 941 ^b	82, 76.1ª, 135 ^b	148, 132.9 ^a , 177 ^b	814, 716.5ª, 914 ^b	389, 359.6 ^a , 441 ^b	7.24
9	Ir	5.25	7.74	618	193	160	295	132	6.07

^a Theoretical Ref. [29].

^b Theoretical Ref. [30].

^c Theoretical Ref. [32].

Table 1 and Supplementary Table S2 present the calculated values of lattice constants (a and c), five independent elastic constants (C_{11} , C_{12} , C_{13} , C_{33} , and C_{44}), and E_{form} for h-MN₆ compounds. Table 1 lists 8 compounds that are both mechanically and dynamically stable, while Supplementary Table S2 has unstable compounds (both mechanically and dynamically unstable compounds, and mechanically stable but dynamically unstable compounds). Fig. 2a and b show volume and E_{form} vs group number, respectively, for all h-MN₆. For 3d block of elements, both the volume and E_{form} does not have a clear trend and is more zigzag. However, both the volume and E_{form} show a parabolic relationship with group number in all 3d, 4d and 5d block elements. This parabolicity is due to the fact that the size of transition metals decrease from initial to intermediate elements and start increasing thereafter [52]. The volume decreases at first and increases finally, whereas the opposite is true for E_{form} . The concave up parabola in E_{form} is due to the fact that when the volume declines in the intermediate transition metals, electrons are more squeezed which require higher energy for stabilization due to Pauli exclusion principle. To determine the mechanical stability of h-MN₆ structures, the following conditions in terms of elastic constants were used [55,76]: $C_{44} > 0$, $C_{11} > |C_{12}|$, and $(C_{11} + 2C_{12})C_{33} > 2C_{13}^2$. In our study, we see that out of 29 h-MN₆ compounds, only 8 (FeN₆, NiN₆, CuN₆, TcN₆ RuN₆, ReN₆, OsN₆, and HgN₆) are mechanically unstable. The calculated values of Bulk modulus (B), shear modulus (G), Young's modulus (E), Vickers hardness (H_V), Pugh's ratio (k), Poisson's ratio (ν), and Debye temperature (θ_D) for all mechanically stable compounds are presented in Tables 2 and S3. All these lattice and elastic parameters are predictive as there is no any experimental work available in h-MN₆. Also, our calculated values match with earlier theoretical work where available like for h-WN₆ [29,30,32].

The values of E_{form} (Tables 1 and S2) for all h-MN₆ are positive. The high volume density of N-N bonds may result in these high formation energies. However, these high positive values do not preclude synthesis of these compounds. As observed for PtN2 [73,77] high temperature or pressure routes of synthesis are feasible and should be explored, which can be associated with the theoretically predicted high pressure of 65 GPa necessary to form h-WN₆ by Xia et al. [29]. However, the formed material will only quench back to the ambient pressure and considered stable only if it is both mechanically as well as thermally stable [34]. For vibrationally stable materials, calculated phonon DOS should not be below zero frequency. Out of 29 h-MN₆ compounds, we found that only 8 of them are vibrationally stable. Supplementary Fig. S1 shows the calculated phonon DOS in the order of increasing hardness from top to bottom for compounds that are both vibrationally and mechanically stable and we observe no phonon DOS below zero frequency. Supplementary Fig. S2 presents the phonon DOS calculations in the order of their increasing hardness from top to bottom for all other mechanically stable compounds showing these materials do not have stable phonon by displaying negative frequencies of phonon DOS. Thus, even though these materials are mechanically stable, they are not thermally stable. Similarly, Supplementary Fig. S3 represents the materials which



Fig. 2. Volume, formation energy and charge transfer vs. group number in all 3d, 4d and 5d $\rm h\text{-}MN_{6}.$

Table 2

Bulk modulus (B), shear modulus (G), Young's modulus (E), Vickers hardness (H_v), Pugh's ratio (k), Poisson's ratio (v), Debye temperature (θ_D), and charge transfer (q_{trans}) in units of elementary charge e, for both vibrationally and mechanically stable h-MN₆.

Gr.	М	B (GPa)	G (GPa)	E (GPa)	H _v (GPa)	k	ν	θ_D (K)	q _{trans}
5	v	217	108	277	11	0.50	0.29	875	1.78
7	Mn	247	158	390	20	0.64	0.24	1020	1.39
9	Co	177	129	311	20	0.73	0.21	908	1.11
12	Zn	158	68	179	7	0.43	0.31	673	1.24
6	Mo	318, 257.9 ^a	311, 268.6 ^a	703	52, 50.6 ^a	0.98	0.13	1224	2.16
5	Та	319	281	652	43	0.88	0.16	968	2.47
6	W	334, 302.7ª, 419.5 ^b	343, 315.7ª, 408.1 ^b	767, 878.5 ^b	59, 56.8ª, 62.2 ^b	1.03	0.12	1051	2.43, 2.4 ^a
9	Ir	266	156	391	18	0.59	0.25	733	1.26

^a Theoretical Ref. [29].

^b Theoretical Ref. [30].

are both mechanically and vibrationally unstable that also display negative phonon DOS frequencies. Hence, our investigation on mechanical as well as vibrational stability revealed that only 8 h-MN₆ (VN₆, MnN₆, CoN₆, ZnN₆, MoN₆, TaN₆, WN₆, and IrN₆) compounds (Table 1) are both mechanically and vibrationally stable, whereas 13 h-MN₆ (ScN₆, TiN₆, CrN₆, YN₆, ZrN₆, NbN₆, RhN₆, PdN₆, AgN₆, CdN₆, HfN₆, PtN₆, and AuN₆) compounds (Table S3) that are mechanically stable but vibrationally unstable.

As both mechanically and vibrationally stable materials are only quenchable to ambient pressure, we want to focus our attention on those 8 h-MN₆ only while discussing their H_V. In our study, we have found that the calculated values of H_V for them range from the lowest value of 7 GPa for ZnN₆ to highest value of 59 GPa for WN₆ with MoN_6 (52 GPa) and TaN_6 (43 GPa) as other two hardest compounds as presented in Table 2. Our value of H_V for WN₆ is little bit higher than the values earlier reported by Xia et al. (57 GPa) and Quan Li et al. (54 GPa). However, the difference in values are well within the range expected with DFT methods [29,30]. Also, the Vickers hardness for MoN₆ (52 GPa) is found close to the value reported by Xia et al. (51 GPa) [29]. Based on our result, we may assert that h-WN₆ could be one of the super-hard compounds after diamond and cubic boron nitride (c-BN) for which the GGA-PBE results are ~94.1 GPa for diamond and ~63.5 GPa for c-BN, respectively [57,78]. Similarly, some other theoretically reported values for hexagonal phase of tungsten nitride like h-WN (24.9 GPa) [29] and h-WN2 (36.6 GPa) [79] along with our calculated value of 59 GPa for h-WN₆ indicate that increasing N concentration would enhance the hardness. It has been established that the elastic constant C₄₄ and hence G give an indication of material's stability to oppose shear strain [39,40,80] and higher value of C_{44} leads to higher value of G and hence higher value of H_V which is true in our study as well. Also, the high values of G observed in h-WN₆ (343 GPa), h-MoN₆ (311 GPa), and h-TaN₆ (281 GPa) indicates that these super-hard materials are stable against the shear deformations. According to Pugh, the material is brittle if k > 0.57 and ductile if $k \le 0.57$ [2,54,81,82]. Our investigation (Table 2) shows that except for h-VN₆ and h-ZnN₆, all other vibrationally and mechanically stable compounds including the super-hard h-MN₆ are brittle in nature. Such exceptional properties including B and E could make super-hard h-MN6 a possible candidate for the hard coating applications.

Furthermore, the study of relationship between calculated values of θ_D , using mechanical properties, and H_V for both mechanically and vibrationally stable h-MN₆ compounds (Supplementary Fig. S4) is in accordance with the prediction of Deus [61] and Miao et al. [83] where they proposed that θ_D and H_V are linearly related as described by Eq. (2). We have calculated the fitting constants through the linear plot shown in Supplementary Fig. S4, and predicted a and b to be 4772.17 $(\text{GPa}^{-1/2}(\text{kg/m}^3)^{1/6}(\text{g/mol})^{1/3}\text{K})$ and 217.46 (K) respectively. Hence, our calculations indicate that θ_D is normally high for high H_V compounds and are always higher than 600 K for both mechanically and vibrationally stable h-MN₆ compounds. According to Lindemann [84], the melting temperature (T_m) of material is related linearly with θ_D as: $\theta_D = aT_m^{1/2}M^{-1/2}V^{-1/3}$, where V is volume of the crystal and a is a constant. This infers the material with high θ_D will have high T_m indicating that our predicted super-hard materials have high T_m and such materials could have prolific industrial use in high temperature applications where materials with high T_m are

Table S4 lists magnetic moments of atomic orbitals found in only 5 h-MN₆ out of 29. In each unit cell, h-FeN₆ has the highest (4.767 μ_B) magnetic moment, whereas h-MnN₆ has the lowest (0.465 μ_B). In all M atoms, s- and p-orbitals have little to negligible contribution to the total magnetic moment of the M atom compared to d-orbital. Similarly, s-orbital has negligible contribution compared to p-orbital in N atoms. Likewise, the total contribution to the magnetic moment of h-MN₆ due to N atoms is negligible in comparison to M atoms except in h-ScN₆, where contribution due to N atoms is three times than due to M atoms.

Interestingly, the magnetic moments are observed only in the $h-MN_6$ where M atoms are from 3d block of transition metals. Out of five magnetic $h-MN_6$, all the M atoms have ferromagnetic character whereas N atoms in $h-FeN_6$ and $h-VN_6$ show anti-ferromagnetic character. Only three (CoN₆, MnN₆ and VN₆) out of five magnetic h-MN₆ are both mechanically and dynamically stable.

3.2. Electronic properties

Hardness of a crystal can be related to the resistance to deformation which is related to the nature of chemical bonds in the crystal [3,85]. The level of ionicity and covalency can be studied through the calculations of charge transfer from M to N ring in h-MN₆ compounds. Our study of Bader charge transfer (qtrans) on both mechanically and vibrationally stable h-MN₆ in Table 2 shows that predicted super-hard compounds have a higher value of charge transfer than the other less harder compounds. Charge transfer vs group number observed in Fig. 2c is consistent with the expectation that charge transfer decreases with increase in group number in all 3d, 4d and 5d block elements. This can be correlated with increase in the d-orbital occupation as we increase the group number. Whenever d-count is less, M atoms may have more opportunity to provide electrons to N atoms than in M atoms with higher d-count because higher d-count M atoms may tend to borrow electrons from the outer valence s-orbital and form a filled d-orbital while forming bonds with N atoms in $h-MN_6$.

Our computed results of LDOS for all 29 h-MN₆ compounds are presented in Supplementary Figs. S5-S7. For both mechanically and vibrationally stable h-MN₆ compounds, it is evident from Supplementary Fig. S5 that for lower hardness material, there is higher number of metallic DOS at or below Fermi level than that for super-hard compounds. As hardness increases, the population of metallic DOS (red line) shifts towards right and for super-hard compounds population of nitrogen DOS (blue line) is higher than population of metallic DOS at or below the Fermi level. This trend of LDOS is also true for only mechanically stable h-MN₆ compounds as shown in Supplementary Fig. S7. Also, a band gap is observed in h-MoN₆ and h-WN₆ by not having the population of LDOS continuing through the Fermi energy. In contrast to the least mechanically stable compounds, the population of metallic DOS is always higher than the nitrogen DOS at Fermi level for both vibrationally and mechanically unstable compounds (Supplementary Fig. S7). For the least mechanically stable compounds, we observe that the LDOS below Fermi level becomes more continuous with increasing hardness as in Supplementary Figs. S5 and S6. However, for unstable compounds LDOS is highly fragmented (Supplementary Fig. S7).

To study the bonding and anti-bonding nature of metal and nitrogen atoms, we performed -pCOHP calculations for all 29 h-MN₆ compounds and results are shown in Supplementary Figs. S8-S10. The Fermi level is set to zero for all these figures. In these plots, the bonding is represented by the positive and anti-bonding is represented by -pCOHP population below the Fermi level. In deep down below the Fermi level all M-N (green line), N-N (blue line), and total (purple line) -pCOHP shows the bonding nature for both vibrationally and mechanically stable compounds. Near the Fermi level, M-N and total -pCOHP of the super-hard compounds are in bonding state and N-N are in anti-bonding state. Direct comparison of LDOS and -pCOHP of hardest compound (h-WN₆) and softest compound (h-ZnN₆) are depicted in Fig. 3. It can be inferred from Fig. 3 (upper panel) that h-WN₆ has lower population of metallic DOS below Fermi energy compared with h-ZnN₆. Also, the COHP comparison (Fig. 3, lower panel) shows that W-N bonding is strong for h-WN₆ from about -5 eV to the Fermi level, however, anti-bonding of Zn-N interaction exist in case of h-ZnN₆. This could be an indication of stronger ionic bonding that leads to higher hardness in h-WN₆ than in h-ZnN₆ as verified by the higher value of q_{tans} for h-WN₆ presented in Table 2.

We have calculated the electronic band structure for all 29 $h-MN_6$ compounds using GGA functional and results are shown in Supplemen-



Fig. 3. Comparison of LDOS and -pCOHP for both vibrationally and mechanically stable compounds with highest (h- WN_6) and lowest (h- ZnN_6) Vickers hardness. The Fermi level is set at 0 eV.



Fig. 4. Band gap energy vs hardness for both vibrationally and mechanically stable h-MN₆ showing super hard compounds have very high band gap.

tary Figs. S11–S13. Our calculated values of band gap for both vibrationally and mechanically stable h- MN_6 shows that h- WN_6 and h- MoN_6 possess high band gap energies of 2.94 eV and 2.81 eV, respectively, all others have zero band gaps. As we have calculated our band gap using GGA functional, the true band gaps may be even higher than this because GGA functional tends to underestimate the band gap [48]. This result can be observed in Fig. 4 and it agrees with Yongjun et al. [57] and Gao et al. [3] where they have suggested that the hardness of a polar crystal is proportional to it band gap. Hence, it is concluded that except two super-hard compounds, all other possess metallic character and studies showed that increase in metallic character decreases material's hardness [86,87]. We calculated the partial density of states (PDOS) for the hardest compound h-WN₆, and the result is shown in Fig. 5 along with the calculated electronic band structure. It shows that W_d and N_p states are hybridized, and they could form strong bonding between M and N thereby leading the higher hardness as observed in h-WN₆.

3.3. Comparison with c-WN₆ structure

We studied the c-WN₆ structure in space group $Im\bar{3}m$ to see the effect of crystal structure on predicted hardness over the same stoichiometric ratio of M and N. The crystal structure of c-MN₆ (in our case M = W) is shown in Fig. 1d where W atoms occupy 2a Wyckoff positions, whereas N atoms occupy 12e Wyckoff positions. The cubic structure does not have a ring like structure of N atoms and every N atom has an end-toend connection with one M atom and one N atom. Similarly, every M atom has 6 nearest neighbor N atoms thereby forming an octahedral coordination. For c-WN₆, the calculated value for bond length of M and N atoms is 2.02 Å and the bond length for N atoms is 1.61 Å with density 6311 kg/m³. The N-N covalent single bond is supposed to provide extra hardness observed in h-WN₆ compound [29] compared to c-WN₆ and it is similar to the results observed in case of transition metal boride [88–91].

We checked the phonon stability for c-WN₆ and found that it is vibrationally stable. The result is shown in Supplementary Fig. S14 where the phonon DOS of h-WN₆ is compared with the phonon DOS of c-WN₆. The phonon DOS for c-WN₆ has less number of peaks found upto 20 THz whereas for h-WN₆, the number of peaks are higher present upto 30 THz. This suggests that h-WN₆ can be harder than c-WN₆ as it can withstand higher vibrational frequencies than the latter. Similarly, the calculated values of elastic constants (C_{11} , C_{12} , and C_{44}) were subjected to the



Fig. 5. Electronic band structure and PDOS for $h-WN_6$ per formula unit. The Fermi level is set at 0 eV.

mechanical stability conditions [92,93]: $C_{11} > C_{12}$, $C_{11} + 2C_{12} > 0$, and $C_{44} > 0$. These conditions are found to be satisfied by our calculated values of elastic constants and hence c-WN₆ is also mechanically stable. Thus, as c-WN6 is both vibrationally and mechanically stable, it can be quenched back to ambient pressure from HPTP conditions of synthesizability [30]. The calculated values of elastic constant (a), B, G, E, H_V, k, v, E_{form} , θ_D and q_{trans} are presented in Supplementary Table S5. Our values match closely with earlier theoretical work [30]. As predicted earlier in this paragraph, the calculated value for H_V (14 GPa) for c-WN₆ is significantly less than the value predicted for h-WN₆. This indicates that the hardness does not only depend on the stoichiometric ratio as discussed earlier but also depends on the crystal structure. This discrepancy in the hardness between two phases can also be attributed to the lower charge transferred in c-WN₆ (1.91e) than in h-WN₆ (2.43e). We also calculated the LDOS of c-WN6 and compared it with the LDOS of h-WN₆ (hardest compound) and h-ZnN₆ (softest compound). This result is presented in Supplementary Fig. S15 and it shows that c-WN₆, like other softer materials discussed earlier, has more population of metallic DOS below the Fermi level. Moreover, the band structure plot along with PDOS (Supplementary Fig. S16) compared with the softest material (h-ZnN₆) shows the metallic nature of c-WN₆ and hybridization of W_d and N_p orbitals that might contribute to the hard behavior of these materials.

4. Conclusion

In summary, we studied 29 nitrogen rich transition metal nitrides MN₆ using DFT based first principles calculations. Of these, only 8 (VN₆, MnN₆, CoN₆, ZnN₆, MoN₆, TaN₆, WN₆, and IrN₆) of them are found to be both mechanically and dynamically stable. The calculation of elastic properties of these h-MN₆ showed that the softest compound has Vickers hardness of 7 GPa (h-ZnN₆) and hardest compound has 59 GPa (h-WN₆). The predicted excellent values of Vickers hardness in 3 compounds h-WN₆ (59 GPa), h-MoN₆ (52 GPa), and h-TaN₆ (43 GPa) indicate that these materials could have the potential to serve as super-hard materials. The estimated value of band gap energy for h-MoN₆ (2.81 eV) and h-WN₆ (2.94 eV) shows their semiconducting nature. We compared h-WN6 to c-WN6 to see the effect of crystal structure on hardness keeping the stoichiometric ratio of M to N same. This study concludes that c-WN₆ is softer material and achieving high hardness is unique to the hexagonal phase only (due to higher number of covalently bonded 6 nitrogen atoms that form hexagonal rings). Also, the investigation of Bader charge analysis reveals that charge transfer in h-WN₆ (2.43e) is higher than that of c-WN₆ (1.91e) pointing ionic bonding in h-WN₆ is stronger. Finally, h-WN₆ has more vibrational frequency than c-WN₆ causing it to be harder. Kaner's [4] idea that higher metallic bonds may lead to lower hardness is consistent with our result seen in Supplementary Fig. S15, where h-ZnN₆ and c-WN₆ both have higher metallic density of states below Fermi energy and they have lower hardness than h-WN₆.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The computational work for this project was performed at Ohio Supercomputer Center [94]. We also thank National Science Foundation Division of Civil, Mechanical, and Manufacturing Innovation through grants 1629239 and 1629230 to support this work.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.mtla.2022.101550.

References

- J. Haines, J.M. Leger, G. Bocquillon, Synthesis and design of superhard materials, Annu. Rev. Mater. Res. 31 (2001) 1–23.
- [2] X. Jiang, J. Zhao, X. Jiang, Correlation between hardness and elastic moduli of the covalent crystals, Comput. Mater. Sci. 50 (7) (2011) 2287–2290.
- [3] F. Gao, et al., Hardness of covalent crystals, Phys. Rev. Lett. 91 (1) (2003) 015502.
 [4] R.B. Kaner, J.J. Gilman, S.H. Tolbert, Designing superhard material, Science 308
- (5726) (2005) 1268–1269.
 [5] D. Gall, et al., Growth of poly- and single-crystal ScN on MgO (001): role of low-enargument of the second state of t
- ergy N²⁺ irradiation in determining texture, microstructure evolution, and mechanical properties, J. Appl. Phys. 84 (1998) 6034–6041.
 [6] H. Holleck, Material selection for hard coatings, J. Vac. Sci. Technol. A 4 (1986)
- 2661.
- [7] V. Adhikari, et al., First-principles study of mechanical and magnetic properties of transition metal (M) nitrides in the cubic M4N structure, J. Phys. Chem. Solids 120 (2018) 197–206.
- [8] S.H. Jhi, et al., Vacancy hardening and softening in transition metal carbides and nitrides, Phys. Rev. Lett. 86 (15) (2001) 3348–3351.

- [9] Z.T.Y. Liu, et al., First-principles investigation of the structural, mechanical and electronic properties of the NbO-structured 3d, 4d and 5d transition metal nitrides, Comput. Mater. Sci. 84 (2014) 365–373.
- [10] S.H. Jhi, et al., Electronic mechanism of hardness enhancement in transition-metal carbonitrides, Nature 399 (1999) 132–134.
- [11] X.J. Chen, et al., Hard superconducting nitrides, Proc. Natl. Acad. Sci. U. S. A. 102 (2005) 3198–3201.
- [12] A.M.Y.Y. Liu, M.L. Cohen, Prediction of new low compressibility solids, Science 245 (4920) (1989) 841–8420.
- [13] S. Kodambaka, et al., Absolute orientation-dependent anisotropic TiN(111) island step energies and stiffnesses from shape fluctuation analyses, Phys. Rev. B 67 (3) (2003).
- [14] J.G. Zhao, et al., Structural phase transition of Cu3N under high pressure, Solid State Commun. 150 (33-34) (2010) 1521–1524.
- [15] S. Kodambaka, et al., Size-dependent detachment-limited decay kinetics of two-dimensional TiN islands on TiN(111), Phys. Rev. Lett. 89 (17) (2002) 176102.
- [16] C. Haihua, et al., Strength and elastic moduli of TiN from radial x-ray diffraction under nonhydrostatic compression up to 45 GPa, J. Appl. Phys. 107 (11) (2010).
- [17] A. Kobayashi, Formation of TiN coatings by gas tunnel type plasma reactivespraying, Surf. Coat. Technol. 132 (2000) 152–157.
- [18] S. Kodambaka, et al., Absolute orientation-dependent TiN(001) step energies from two dimentional equilibrium island shape and coarsening measuremnets on epitaxial TiN(001) layers, Surf. Sci. 513 (2002) 468–474.
- [19] S. Kodambaka, et al., Determination of absolute orientation-dependent TiN(001) and TiN(111) step energies, Vacuum 74 (3-4) (2004) 345–351.
- [20] D. Ruopeng, et al., Optical and transport measurement and first-principles determination of the ScN band gap, Phys. Rev. B 91 (4) (2015) 045104p1–045104p12.
- [21] C.S. Shin, et al., Vacancy hardening in single-crystal TiNx(001) layers, J. Appl. Phys. 93 (10) (2003) 6025–6028.
- [22] J. Bareño, et al., Orientation-dependent mobilities from analyses of two-dimensional TiN(111) island decay kinetics, Thin Solid. Films 510 (1-2) (2006) 339–345.
- [23] S. Kodambaka, et al., Absolute TiN(111) step energies from analysis of anisotropic island shape fluctuations, Phys. Rev. Lett. 88 (14) (2002) 146101.
- [24] J. Bareño, et al., TiN surface dynamics role of surface and bulk mass transport processes, in: Am. Inst. Phys., 885, 2007, pp. 205–224.
- [25] Z. Xiuquan, G. Daniel, V. Khare Sanjay, Mechanical properties and electronic structure of anti-ReO3 structured cubic nitrides, M3N, of d block transition metals M: An ab initio study, J. Alloy. Compd. 595 (2014) 80–86.
- [26] S.K.R. Patil, et al., Mechanical stability of possible structures of PtN investigated using first-principles calculations, Phys. Rev. B 73 (10) (2006).
- [27] S. Kodambaka, et al., Nucleation and growth kinetics of spiral steps on TiN(111): anin situlow-energy electron microscopy study, J. Appl. Phys. 98 (3) (2005).
- [28] H.J. McSkimin, W.L. Bond, Elastic moduli of diamond, Phys. Rev. 105 (1) (1957) 116–121.
- [29] X. Kang, et al., A novel superhard tungsten nitride predicted by machine-learning accelerated crystal structure search, Sci. Bull. 63 (13) (2018) 817–824.
- [30] L. Qian, et al., New multifunctional tungsten nitride with energetic N6 and extreme hardness predicted from first principles, EPL 118 (4) (2017) 46001p1–46001p5 Europhysics Letters.
- [31] S.V. Khare, T.L. Einstein, N.C. Bartelt, Dynamics of step doubling simulations for a simple model and comparison with experiment, Surf. Sci. 339 (1995) 353–362.
- [32] K. Xia, et al., A novel superhard tungsten nitride predicted by machine-learning accelerated crystal structure search, Sci. Bull. 63 (13) (2018) 817–824.
- [33] Z. Zhao, et al., Nitrogen concentration driving the hardness of rhenium nitrides, Sci. Rep. 4 (2014) 4797.
- [34] Z. Zhonglong, et al., Potentially superhard hcp CrN2 compound studied at high pressure, Phys. Rev. B 93 (21) (2016).
- [35] N.J. Szymanski, et al., Unconventional superconductivity in 3d rocksalt transition metal carbides, J. Mater. Chem. C 7 (40) (2019) 12619–12632.
- [36] V. Adhikari, et al., First principles investigation into the phase stability and enhanced hardness of TiN-ScN and TiN-YN alloys, Thin Solid. Films 688 (2019) 137284p1-137284p12.
- [37] B.B. Dumre, et al., Improved optoelectronic properties in CdSexTe1-x through controlled composition and short-range order, Sol. Energy 194 (2019) 742–750.
- [38] B.B. Dumre, D. Gall, S.V. Khare, Stability, and electronic and optical properties of ternary nitride phases of MgSnN2: a first-principles study, J. Phys. Chem. Solids 153 (2021).
- [39] G. Kresse, J. Furthmuller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Phys. Rev. B 54 (1996) 11169.
- [40] G. Kresse, J. Furthmuller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, Comput. Mater. Sci 6 (1996) 15–50.
- [41] G. Kresse, J. Hafner, Ab initio molecular-dynamics simulation of the liquid-metal-amorphous-semiconductor transition in germanium, Phys. Rev. B Condens. Matter 49 (20) (1994) 14251–14269.
- [42] G. Kresse, J. Hafner, Ab initio molecular dynamics for liquid metals, Phys. Rev. B Condens. Matter 47 (1) (1993) 558–561.
- [43] P.P. Gunaicha, et al., Structural, energetic and elastic properties of Cu₂ZnSn(S_xSe_{1-x})₄ (x=1, 0.75, 0.5, 0.25, 0) alloys from first-principles computations, Sol. Energy 102 (2014) 276–281.
- [44] W. Yuejian, et al., Thermal equation of state of silicon carbide, Appl. Phys. Lett. 108 (6) (2016) 061906-1–061906-5.
- [45] P.E. Blochl, Projector augmented-wave method, Phys. Rev. B Condens. Matter 50 (24) (1994) 17953–17979.
- [46] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, Phys. Rev. B 59 (1999) 1758–1775.

- [47] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 77 (1996) 3865–3868.
- [48] B.B. Dumre, S.V. Khare, Interrelationship of bonding strength with structural stability of ternary oxide phases of MgSnO3: a first-principles study, Phys. B (2022) 413896.
- [49] J.A. Warner, et al., Ab initio calculations for properties of MAX phases Ti2TlC, Zr₂TlC, and Hf₂TlC, Appl. Phys. Lett. 88 (10) (2006).
- [50] J. Nanke, et al., An ab initio computational study of pure Zn3N2 and its native point defects and dopants Cu, Ag and Au, Thin Solid. Films 564 (2014) 331–338.
- [51] J.L. Roehl, et al., Binding sites and diffusion barriers of a Ga adatom on the GaAs(001)-c(4×4) surface from first-principles computations, Phys. Rev. B 82 (16) (2010).
- [52] I. Khatri, et al., Correlating structure and orbital occupation with the stability and mechanical properties of 3d transition metal carbides, J. Alloy. Compd. 891 (2022) 161866p1–161866p11.
- [53] J. Anubhav, et al., Commentary: the materials project: a materials genome approach to accelerating materials innovation, APL Mater. 1 (1) (2013) 011002-1–011002-11.
- [54] W. Qun, et al., High-pressure phases and pressure-induced phase transition of MoN6 and ReN6, Phys. Lett. A 383 (20) (2019) 2429–2435.
- [55] W. Zhi-jian, et al., Crystal structures and elastic properties of superhard IrN2 and IrN3 from first principles, Phys. Rev. B 76 (5) (2007) 054115-1–054115-15.
- [56] R. Hill, The elastic behaviour of a crystalline aggregate, Proc. Phys. Soc. 65 (1952) 349–354.
- [57] T. Yongjun, X. Bo, Z. Zhisheng, Microscopic theory of hardness and design of novel superhard crystals, Int. J. Refract. Met. Hard Mater. 33 (2012) 93–106.
- [58] Z.T. Liu, et al., Structural, mechanical and electronic properties of 3d transition metal nitrides in cubic zincblende, rocksalt and cesium chloride structures: a first-principles investigation, J. Phys. Condens. Matter 26 (2) (2014) 025404.
- [59] T.R. Stefan, K. Manja, First principles density functional theory prediction of the crystal structure and the elastic properties of Mo2ZrB2 and Mo2HfB2, Crystals 10 (10) (2020) 865p1–865p14.
- [60] W. Bao, D. Liu, Y. Duan, A first-principles prediction of anisotropic elasticity and thermal properties of potential superhard WB3, Ceram. Int. 44 (12) (2018) 14053–14062.
- [61] P. Deus, H.A. Schneider, Estimation of the debye temperature of diamond-like semiconducting compounds from bulk modul and microhardness, Cryst. Res. Technol. 18 (1983) 491–500.
- [62] T. Atsushi, T. Isao, First principles phonon calculations in materials science, Scr. Mater. 108 (2015) 1–5.
- [63] M. Yu, D.R. Trinkle, Accurate and efficient algorithm for Bader charge integration, J. Chem. Phys. 134 (6) (2011) 064111.
- [64] W. Tang, E. Sanville, G. Henkelman, A grid-based Bader analysis algorithm without lattice bias, J. Phys. Condens. Matter 21 (8) (2009) 084204.
- [65] E. Sanville, et al., Improved grid-based algorithm for Bader charge allocation, J. Comput. Chem. 28 (5) (2007) 899–908.
- [66] H. Graeme, A. Andri, J. Hannes, A fast and robust algorithm for Bader decomposition of charge density, Comput. Mater. Sci. 36 (3) (2006) 354–360.
- [67] N.J. Szymanski, et al., Prediction of improved magnetization and stability in Fe16N2 through alloying, J. Appl. Phys. 126 (9) (2019).
- [68] Z.T.Y. Liu, D. Gall, S.V. Khare, Electronic and bonding analysis of hardness in pyritetype transition-metal pernitrides, Phys. Rev. B 90 (13) (2014).
- [69] V.L. Deringer, A.L. Tchougreeff, R. Dronskowski, Crystal orbital hamilton population (COHP) analysis as projected from plane-wave basis sets, J. Phys. Chem. A 115 (21) (2011) 5461–5466.
- [70] R. Dronskowski, P.E. Bloch, Crystal orbital hamilton populations (COHP). energy-resolved visualization of chemical bonding in solids based on density-functional calculations, J. Phys. Chem. 97 (33) (1993) 8617–8624.
- [71] S. Maintz, et al., LOBSTER: a tool to extract chemical bonding from plane-wave based DFT, J. Comput. Chem. 37 (11) (2016) 1030–1035.
- [72] S. Maintz, M. Esser, R. Dronskowski, Efficient Rotation of Local Basis Functions Using Real Spherical Harmonics, Acta Phys. Pol. B 47 (4) (2016).
- [73] J.C. Crowhurst, et al., Synthesis and characterization of the nitrides of platinum and iridium, Science 311 (5765) (2006) 1275–1278.
- [74] R. Yu, Q. Zhan, X.F. Zhang, Elastic stability and electronic structure of pyrite type PtN2: a hard semiconductor, Appl. Phys. Lett. 88 (5) (2006) 051913-1–051913-3.
- [75] C. Yongjin, B. Shuhong, High energy density material (HEDM) progress in research azine energetic compounds, Johns Matthey Technol. Rev. 63 (1) (2019) 51–72.
- [76] C.M. Kube, M. Jong, Elastic constants of polycrystals with generally anisotropic crystals, J. Appl. Phys. 120 (16) (2016) 165105-1–165105-14.
- [77] E. Gregoryanz, et al., Synthesis and characterization of a binary noble metal nitride, Nat. Mater. 3 (2004) 294–297.
- [78] B. Li, H. Sun, C. Chen, Large indentation strain-stiffening in nanotwinned cubic boron nitride, Nat. Commun. 5 (2014) 4965.
- [79] W. Hui, et al., Ultra-incompressible phases of tungsten dinitride predicted from first principles, Phys. Rev. B 79 (13) (2009).
- [80] S.K.R. Patil, et al., Super hard cubic phases of period VI transition metal nitrides: first principles investigation, Thin Solid. Films 517 (2) (2008) 824–827.
- [81] S.F. Pugh, Relations between the elastic moduli and the plasctic properties of polycrystaline pure metals, Philos. Mag. J. Sci. 45 (1954) 823–843.
 [82] A. Mansouri Tehrani, et al., Machine learning directed search for ultraincompress-
- [82] A. Mansouri Tehrani, et al., Machine learning directed search for ultraincompress ible, superhard materials, J. Am. Chem. Soc. 140 (31) (2018) 9844–9853.
- [83] N.H. Miao, et al., Theoretical investigation on the transition metal borides with Ta3B4-type structure a class of hard and refractory material, Comput. Mater. Sci 50 (2011) 1559–1566.
- [84] F.A. Lindmann, The calculation of molecular vibration frequencies, Phys. Z. 11 (1910) 609–612.

- [85] W.D. Nix, H. Gao, Indentation size effects in crystalline materials A law for strain gradient plasticity, J. Mech. Phys. Solids 46 (1998) 411–425. [86] G. Xiaoju, et al., Hardness of covalent compounds: roles of metallic component and
- d valence electrons, J. Appl. Phys. 104 (2) (2008).
 [87] W. Qianqian, et al., Is orthorhombic iron tetraboride superhard? J. Materiom. 1 (1)
- (2015) 45-51.
- [88] B. Levine Jonathan, H. Tolbert Sarah, B. Kaner Richard, Advancements in the search for superhard ultra-incompressible metal borides, Adv. Funct. Mater. 19 (22) (2009) 3519-3533.
- [89] Z. Chenpeng, et al., Indentation strength of ultraincompressible rhenium boride, carbide, and nitride from first-principles calculations, Phys. Rev. B 86 (1) (2012) 014108-1-014108-9.
- [90] L. Bing, et al., Fundamental constraints on the strength of transition-metal borides: the case of CrB4, Phys. Rev. B 87 (17) (2013) 174106-1-174106-7.
- [91] M.T. Yeung, R. Mohammadi, R.B. Kaner, Ultraincompressible superhard materials, Annu. Rev. Mater. Res. 46 (2016) 465-485.
- [92] J.F. Nye, Physical Properties of Crystals: Their Representation by Tensors and Matrices, Oxford Science Publications, 1985.
- [93] F. Mouhat, F.X. Coudert, Necessary and sufficient elastic stability conditions in various crystal systems, Phys. Rev. B 90 (22) (2014) 224104-1-224104-4.
- [94] Ohio Supercomputer Center. 1987.
 [95] M. Koichi, I. Fujio, VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data, J. Appl. Crystallogr. 44 (6) (2011) 1272–1276.