Elastic and thermodynamic properties of vanadium nitride under pressure and the effect of metallic bonding on its hardness*

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By the particle-swarm optimization method, it is predicted that tetragonal $P4_2mc$, $I4_1md$, and orthorhombic $Amm2$ phases of vanadium nitride (VN) are energetically more stable than NaCl-type structure at 0 K. The enthalpies of the predicted three new VN phases, along with WC, NaCl, AsNi, CsCl type structures, are calculated each as a function of pressure. It is found that VN exhibits the WC-to-CsCl type phase transition at 256 GPa. For the considered seven crystallographic VN phases, the structures, elastic constants, bulk moduli, shear moduli, and Debye temperatures are investigated. Our calculated equilibrium structural parameters are in very good agreement with the available experimental results and the previous theoretical results for the NaCl phase. The Debye temperatures of VN predicted three novel phases, which are all higher than those of the remaining structures. The elastic constants, thermodynamic properties, and elastic anisotropies of VN under pressure are obtained and the mechanical stabilities are analyzed in detail based on the mechanical stability criteria. Moreover, the effect of metallic bonding on the hardness of VN is also investigated, which shows that VNs in $P4_2mc$, $I4_1md$, and $Amm2$ phases are potential superhard phases. Further investigation on the experimental level is highly recommended to confirm our calculations presented in this paper.

Keywords: vanadium nitride, elastic constants, thermodynamic properties, hardness

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1. Introduction

Transition-metal nitrides have received more attention as powerful candidates of superhard materials and potential technological applications.[1–5] There are lots of theoretical and experimental efforts devoted to the transition-metal nitrides. Vanadium nitride (VN) adopting the NaCl type structure has been a leading subject of many investigations on such transition-metal compounds because of its high melting temperature, electrical conductivity, and chemical stability.[6,7] However, phonon anomalies have been observed in substoichiometric NaCl type VN_x ($x < 1.0$) at the X point of the Brillouin zone (BZ) by inelastic neutron diffraction measurements.[8] In addition, the phonon spectrum calculations of VN at 0 K revealed that this compound is dynamically instable.[9] The stoichiometric VN was found to be able to enhance the stability in the WC type structure as compared with the NaCl type structure based on the total energy calculation with the first-principles method.[10] It is also found that the total energy of AsNi and tetragonal ($P4_2/mcm$) phases is lower than that of NaCl phase at 0 K and 0 GPa. The stabilization of the NaCl type over WC type transition-metal compounds with nitrogen vacancies has only been detected in experiment. Meanwhile, tetragonal and triclinic phases have also been detected in experiment.[11] In addition, VN was predicted to undergo a structural transition from NaCl to CsCl type arrangement under high pressure.[12] Despite the amount of experimental and theoretical information accumulated on VN, to our knowledge, the structural and thermodynamic properties of VN in various structures have not yet been well understood, especially under high pressure. In order to fully exploit this material, it is necessary to search for the new phases of stoichiometric VN in the framework of a first-principles approach in order to obtain a good understanding of the physical properties of VN in various phases, in particular of its structural and thermodynamic properties under high pressure.

In the present paper, the tetragonal $P4_2mc$, $I4_1md$, and orthorhombic $Amm2$ phases of VN are predicted to be energetically more stable than NaCl type structure with increasing pressure. We describe the structure properties and the phase transition of VN in the predicted three novel phases, along

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with WC, NaCl, AsNi, and CsCl type structures, by the first-principles calculations. Our purpose is to give comprehensive information about the structures and mechanical properties of VN, and to further understand the thermodynamic properties of VN in various structures under high pressure. On the other hand, we also aim to provide powerful guidelines for future experimental investigations and we hope that such investigations can contribute to further understanding of the hardness of VN in considered structures.

2. Computational methods

In our calculations, candidate structure searches of stoichiometric VN are performed at 0 K using the particle-swarm optimization (PSO) method.[13] The first-principles calculations are performed based on the density functional theory packaged in Cambridge Serial Total Energy Package (CASTEP).[14] Conventional unit cells are used for studying seven structures of VN in the geometry optimization process. For the electronic and elastic-constant calculations, Norm-conserving pseudpotential[15] are used and the exchange–correlation terms are considered by the Perdew–Berke–Ernzerhof (PBE) form of the generalized gradient approximation (GGA). While for the hardness calculations, the Ultrasoft Vanderbilt pseudpotential[16] are used instead. During the structure optimizations, the total energy is minimized by optimizing both the cell parameters and the atomic positions. All forces on atoms are less than 0.01 eV/Å and a self-consistent field tolerance of 2.0×10^{-6} eV is used. To ensure that our calculations are accurate, the plane-wave cutoff energy is 850 eV and 500 eV for Norm-conserving potential and Ultrasoft Vanderbilt potential, respectively. The following set of k points is generated using a Monkhorst–Pack scheme:[17] $17\times17\times14$ and $16\times16\times8$ for hexagonal WC and AsNi phases, respectively, $16\times16\times16$ for cubic NaCl and CsCl phases, $14\times14\times14$ for tetragonal $P4_2mc$, $13\times13\times12$ for orthorhombic $Amm2$, and $13\times13\times17$ for tetragonal $I4_1md$. Formation enthalpy (ΔH) for VN is calculated from

$$\Delta H = H(\mathrm{VN}) - H(\mathrm{V}) - 1/2H(\mathrm{N_2}),$$

where the solid molecular N_2 is considered as the chemical potential reference. The hardness of diamond is also calculated for comparison.

3. Results and discussion

3.1. Formation enthalpy and pressure-induced structural phase transition

In order to obtain a deep insight into the phase stability of VN, the thermodynamic stabilities of various VN structures, each as a function of pressure, are investigated by calculating the formation enthalpies. The pressure dependences of enthalpy for several structures are shown in Fig. 1. Among the considered structures, VN in the WC structure type is energetically the most stable, which is consistent with previous calculated result.[9] In addition, it is found that at zero pressure the enthalpies of tetragonal $P4_2mc$, $I4_1md$, and orthorhombic $Amm2$ phases are all lower than that of NaCl type phase and they exist as new metastable phases. The relative stability order of these seven VN structures considered is WC type $> P4_2mc > Amm2 > I4_1md >$AsNi type $>$ NaCl type $>$ CsCl type at zero pressure. This sequence indicates that WC type has enhanced stability in the considered structures at a temperature close to 0 K. The calculations show that VN will undergo a structural phase transition from the WC phase to the CsCl phase as pressure increases. Two enthalpy curves imply that the WC phase-to-CsCl transition occurs at 256 GPa. As far as we know, there are no experimental results available for comparison that are related to the WC-CsCl structural phase transition. We notice that the transition pressure from NaCl to CsCl phase is about 110 GPa. This result is smaller than 189 GPa from the work of Hao *et al.*,[12] owing to the difference between the calculation method and pseudpotential used.

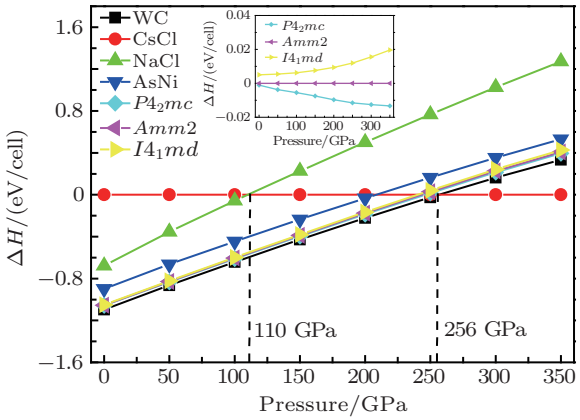


Fig. 1. (color online) Enthalpy as a function of pressure for VN in WC, CsCl, NaCl, AsNi, $P4_2mc$, $Amm2$, and $I4_1md$ structures at $T = 0$ K, where the WC structure is taken as the reference. Inset shows the enthalpy of $P4_2mc$, $Amm2$, and $I4_1md$ as a function of pressure, where the $Amm2$ structure is taken as the reference.

3.2. Structural properties

The structural properties are very important for understanding the solid properties from the microscopic viewpoint. Seven structures of VN, e.g. WC, AsNi, NaCl, CsCl, $P4_2mc$, $Amm2$, and $I4_1md$ phases, are simulated using the first-principles calculations. The calculated structural parameters, that is, elastic constants, formation enthalpies per formula unit (ΔH/f.u.), the values of bulk modulus (B), shear modulus (G), Young's modulus (E), Poisson's ratio (ν), and Debye temperature (Θ_D) are listed in Table 1. For comparison, one can note that our optimized lattices are in good agreement with the experimental value of 4.133 Å (within 0.5%) for NaCl type structure and close to the previous theoretical data for WC, AsNi, and CsCl type phases.[9] Furthermore, for the NaCl type

phase, the previous studies gave the bulk modulus an experimental value of 268 GPa and a theoretical value of 303 GPa, which are in excellent agreement with our calculated value of 298 GPa. Our calculated elastic constants are also reasonable compared with the experimental and previous theoretical values, indicating that our calculations are valid and believable. According to the quasi-harmonic Debye model, we give an estimation of Debye temperature from the average sound velocity. However, for the new predicted three metastable $P4_2mc$, $Amm2$, and $I4_1md$ phases, there are neither experimental nor theoretical values available for use as a reference for our calculated values. In this work, we find that these three structures have the same bulk modulus and that their Debye temperatures are all higher than those of the remaining structures. We hope that our results can serve as a guidance for future experimental investigations.

Table 1. Calculated lattice constants, a, b, and c (Å), cell volume per formula unit V (Å^3), and formation enthalpy per formula unit ΔH (eV), bulk modulus B (GPa), shear modulus G (GPa), Young's modulus E (GPa), Poisson's ratio ν, and Debye temperature Θ_D (K) at the Norm-conserving pseudopotential method for VN from various space groups: hexagonal (WC type, $P\bar{6}m2$, No. 187; AsNi type, $P6_3/mmc$, No. 194), cubic (NaCl type, $Fm\bar{3}m$, No. 225; CsCl type, $Pm\bar{3}m$, No. 221), tetragonal ($P4_2mc$, No. 105; $I4_1md$, No. 109), and orthorhombic ($Amm2$, No. 38) phases.

	WC	NaCl	CsCl	AsNi	$P4_2mc$	$Amm2$	$I4_1md$
a	2.763	4.153, 4.133[a], 4.13[b]	2.562	2.793	2.699	2.716	2.699
b						2.684	
c	2.656			5.204	9.611	14.424	9.622
ΔH	–2.259	–1.833, –2.0[c]	–1.161	–2.059	–2.221	–2.220	–2.215
V	17.552	17.902	16.807	17.582	17.515	17.524	17.528
C_{11}	550	514, 591[b], 533[d]	846	540	708	675	712
C_{22}						746	
C_{33}	810			676	572	582	585
C_{44}	250	108, 137[b], 133[d]	140	179	216	226	219
C_{55}						206	
C_{66}						264	
C_{12}	184	189, 159[b], 135[d]	13	180	128	128	131
C_{13}	129			143	138	138	130
C_{23}						131	
B	308	298, 303[b], 268[d]	291	298	310	310	310
G	229	128, 164[b]	221	192	243	243	247
E	551	336, 417[b]	529	474	578	578	586
ν	0.202	0.312, 0.270[b]	0.197	0.235	0.189	0.189	0.185
Θ_D	974	739	949	894	1001	1002	1009

[a]Ref. [18], [b]Ref. [19], [c]Ref. [20], [d]Ref. [21]

3.3. Pressure dependence of elastic and thermodynamic properties

The elastic constants of solids provide a link between the mechanical and dynamical behavior of crystals, and give important information about the nature of the force operation in solids. Using the pressure dependence of elastic constant, one can judge the mechanical stability of a crystal under high pressure. The Born mechanical stability criteria for hexagonal, cubic, tetragonal, and orthorhombic crystal are given as follows:[22]

for hexagonal phase (C_{11}, C_{12}, C_{13}, C_{33}, C_{44})

$$C_{44} > 0, \quad C_{11} > C_{12}, \quad (C_{11} + 2C_{12})C_{33} > C_{13}^2;$$

for cubic phase (C_{11}, C_{12}, C_{44})

$$C_{11} > 0, \quad C_{44} > 0, \quad C_{11} > |C_{12}|, \quad (C_{11} + 2C_{12}) > 0;$$

for tetragonal phase (C_{11}, C_{12}, C_{13}, C_{33}, C_{44}, C_{66})

$$C_{11} > 0, \quad C_{33} > 0, \quad C_{44} > 0, \quad C_{66} > 0,$$
$$C_{11} - C_{12} > 0, \quad (C_{11} + C_{33} - 2C_{13}) > 0,$$
$$(2(C_{11} + 2C_{12}) + C_{33} + 4C_{13} > 0;$$

for orthorhombic phase (C_{11}, C_{12}, C_{13}, C_{23}, C_{22}, C_{33}, C_{44}, C_{55}, C_{66})

$$C_{ii} > 0 \quad (i = 1-6),$$
$$C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23}) > 0,$$
$$(C_{11} + C_{22} - 2C_{12}) > 0,$$
$$(C_{11} + C_{33} - 2C_{13}) > 0, \quad C_{22} + C_{33} - 2C_{23} > 0.$$

Figure 2 shows the hydrostatic pressure dependences of elastic constants of VN for the considered structures. It is found that the hexagonal WC and AsNi type VN satisfy the stability conditions when the pressures increase up to 300 GPa and 250 GPa, respectively. The two hexagonal phases have the same tendency as the five elastic constants in their stable pressure ranges. They are in the sequence: $C_{33} > C_{11} > C_{44}$ and $C_{12} > C_{13}$, implying that the atomic bonds along the [001] direction between the nearest neighbors are stronger

than along the [100] direction. It is obvious that the cubic NaCl type structure is stable only as pressure increases up to 125 GPa, and the CsCl type VN is stable at least as pressure increases above 256 GPa. Our first-principles calculations have given the same tendency of the three elastic constants $C_{11} > C_{12} > C_{44}$ for the two cubic VN phases, with their stable pressure range taken into account. C_{11} is more sensitive to the change of pressure than other two elastic constants. The large value of C_{11} reflects the strong covalent bonds between the vanadium d-like states and the nitrogen p-like states along the [100] direction. The elastic constants for tetragonal $P4_2mc$ and $I4_1md$ VN phases increase monotonically with the increasing of pressure except for C_{44}. While the variation of elastic constant C_{44} decreases gradually with pressure increasing. For the $Amm2$ phase, the slopes of C_{11}, C_{22}, and C_{33} become higher than those of C_{55} and C_{66} with increasing pressure. Thus, the elastic constant C_{44} shows the same changing tendency for $P4_2mc$ and $I4_1md$ phases. The new predicted three phases all satisfy mechanical stable conditions until the pressure goes up to 300 GPa, suggesting that the orthorhombic $Amm2$ phase of VN is unstable when $P > 300$ GPa. From Fig. 3 it follows that pressure has an important influence on bulk modulus, shear modulus, and Debye temperature. The bulk moduli of seven VN structures increase linearly in a similar slope with pressure increasing, indicating that it is difficult to compress with pressure increasing. This feature has been reported by Hao *et al.*[12] for the NaCl phase. The variation of shear modulus in CsCl type with increasing pressure is higher than those of other structures among the considered VN structures. The variation of Debye temperature with pressure has the same tendency as the variation of shear modulus with pressure, showing that the anisotropies of the different VN structures all increase with increasing pressure.

A proper description of an anisotropic behavior has an important implication in crystal physics. The shear anisotropic factor provides a measure of the degree of anisotropy in the bonding between atoms in different planes. The anisotropic factors of VN in WC, AsNi, NaCl, CsCl, $P4_2mc$, $Amm2$, and $I4_1md$ phases are plotted in Fig. 4, each as a function of pressure. For hexagonal crystal, the elastic anisotropy Δp, Δs_1, and Δs_2 can be expressed as $\Delta p = C_{33}/C_{11}$, $\Delta s_2 = 2C_{44}/(C_{11} - C_{12})$, $\Delta s_1 = (C_{11} + C_{33} - 2C_{13})/4C_{44}$,[23] where Δp, Δs_1, and Δs_2 are the anisotropies for the compression p-wave and two shear s-waves, respectively. As shown in Fig. 4, Δp has no remarkable change, and the changes of Δs_1 and Δs_2 go in the opposite directions for both hexagonal WC and AsNi type VN. The anisotropy of elasticity is measured by $A = 2C_{44}/(C_{11} - C_{12})$ for cubic crystals. A decreases in NaCl and increases in CsCl type structures with pressure increasing. For the orthorhombic structures, the anisotropic factors for the shear planes $\{100\}$, $\{010\}$, and $\{001\}$ are written as[24] $A_1 = 4C_{44}/(C_{11} + C_{33} - 2C_{13})$, $A_2 = 4C_{55}/(C_{22} + C_{33} - 2C_{23})$, and $A_3 = 4C_{66}/(C_{11} + C_{22} - 2C_{12})$. It is interesting to note that there is little difference between A_1 and A_2 while A_3 increases with pressure for the $Amm2$ phase. The shear anisotropic factors of tetragonal VN for $\{100\}$ and $\{001\}$ shear planes are defined as follows:[25] $A_1 = 2C_{66}/(C_{11} - C_{12})$ and $A_2 = 4C_{44}/(C_{11} + C_{33} - 2C_{13})$. We find that A_2 nearly keeps constant and A_1 increases sharply for both tetragonal $P4_2mc$ and $I4_1md$ VN phases with the increasing of pressure.

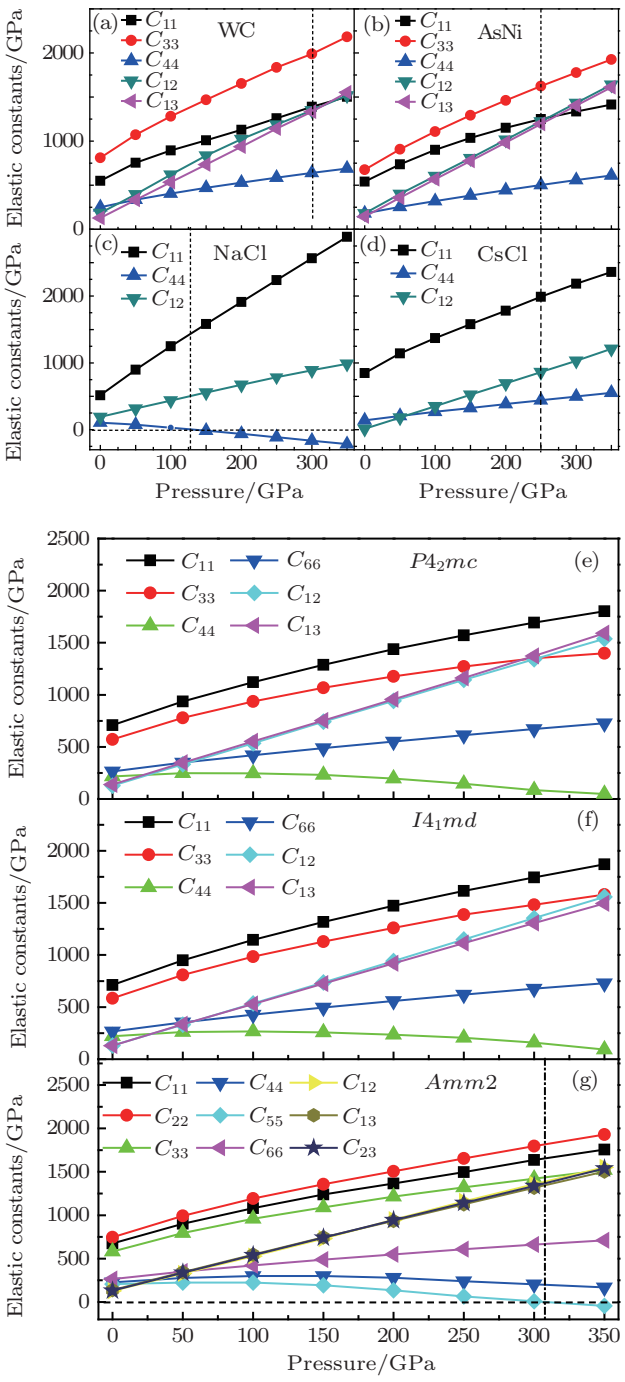


Fig. 2. (color online) Pressure dependences of elastic constants in (a) WC type, (b) AsNi type, (c) NaCl type, (d) CsCl type, (e) $P4_2mc$, (f) $I4_1md$, and (g) $Amm2$ structures of VN.

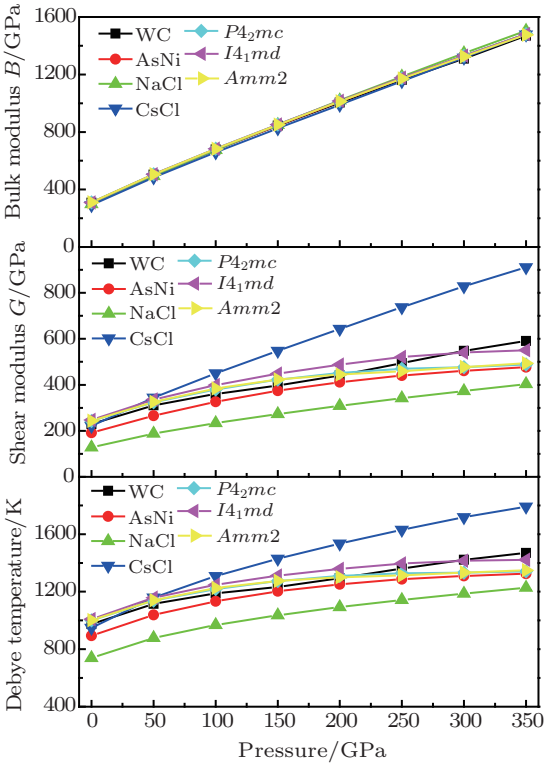


Fig. 3. (color online) Pressure dependences of the bulk modulus B, shear modulus G, and Debye temperature Θ_D in WC, CsCl, NaCl, AsNi, $P4_2mc$, $Amm2$, and $I4_1md$ structures of VN.

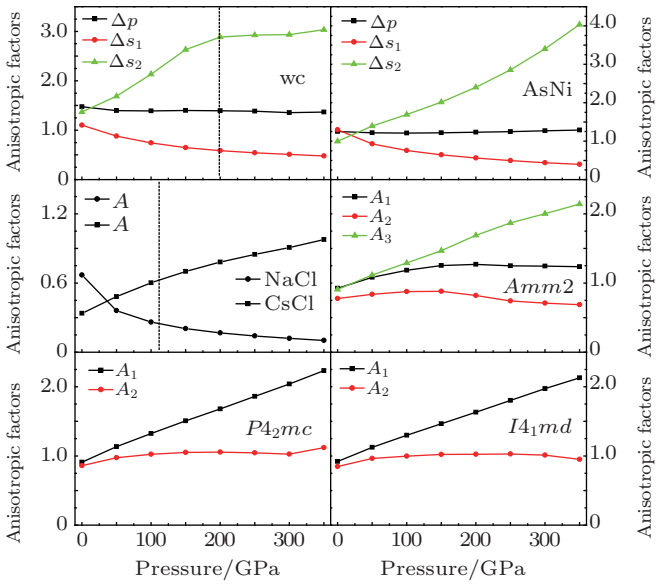


Fig. 4. (color online) Pressure dependences of the anisotropic factors in WC, CsCl, NaCl, AsNi, $P4_2mc$, $Amm2$, and $I4_1md$ structures of VN.

3.4. Density of states and hardness

The band structure and density of states of the WC type VN are presented in Fig. 5. The band structure of Fig. 5(a) indicates that the WC type VN is metallic. The density of states (DOS) of Fig. 5(b) follows the strong hybridization between N and V states with the energy position. Furthermore, the bonding and antibonding states are composed of N 2p and V 4d orbitals. The DOS suggests that the chemical bond between N and V atoms is mainly covalent, with partial iconicity and metallic contributions. It can be seen from Fig. 5 that there is a deep valley E_p at the left of the Fermi level, which is termed a pseudogap. This suggests that not all of the bonding states are filled and that the electrons above E_p become delocalized.

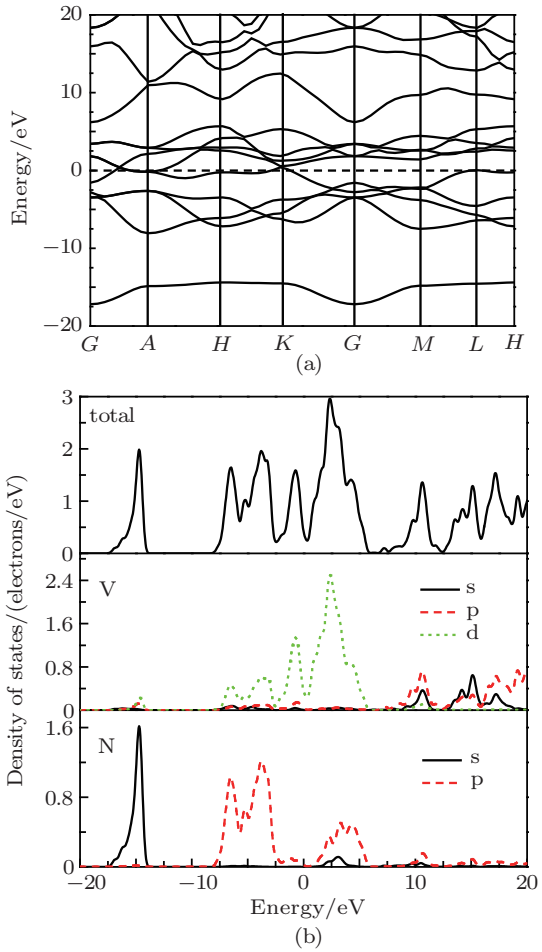


Fig. 5. (color online) (a) Band structure. (b) DOS and PDOS of WC–VN.

On the other hand, the prediction of the hardness of VN as a superhard material is of great potential interest. The estimation of the hardness of nonmetallic materials has been developed by Mulliken population[26] in the first-principles techniques. Since the metallic bonding is delocalized and not directly related to hardness, the hardness calculation should be corrected. Here the correction of the hardness for the compound crystals with metallic bonding is expressed as $H_v(\text{GPa}) = 740(M_P - M'_P)v_b^{-3/5}$, where M_P is the Mulliken population, M'_P is the metallic population, and v_b is the volume of the bond. The metallicity of crystals can be defined as $f_m = M_P/M'_P$. The calculated hardness values of VN in various structures and diamond are listed in Table 2. The metallicity of VN in NaCl type VN structure is 0.46, and its hardness is 17.1 GPa, which are in good agreement with the experimental results[27] as well as with the previous theoretical results.[29] The calculated hardness of diamond is 97.8 GPa, which has an

excellent consistency with the experimental result 100 GPa, indicating that our calculations are reliable. The hardness values of $P4_2mc$, $Amm2$, and $I4_1md$ structures are 19.5, 28.8, and 19.8 GPa, respectively, which are higher than those of WC, AsNi, and NaCl type VN structures. When we take Jiang *et al.*'s empirical formula[30] to evaluate the hardness values of VN in various structures according to the bulk moduli and shear moduli, we find that the results from the Mulliken population method are closer to the experimental values in evaluating the hardness values of metallic bonding compounds. We hope that our work is useful for understanding the effects of metallic bonding on the hardness values of VN in various structures.

Table 2. Calculated hardness values of VN in WC, CsCl, NaCl, AsNi, $P4_2mc$, $Amm2$, and $I4_1md$ structures and diamond. Structure data are cited from the results of GGA of ultrasoft pseupotential method, where $H_{\mathrm{v\ cal}}$ (GPa) and $H_{\mathrm{v\ exp}}$ (GPa) are the calculated and experimental hardness, respectively. d (Å) is the V–N bond length and v_{b} (Å^3) is the bond volume.

	d	M_{P}	M'_{P}	f_{m}	v_{b}	$H_{\mathrm{v\ cal}}$	$H_{\mathrm{v\ exp}}$
Diamond	1.544	0.750			2.835	97.8	100.6[a]
WC	2.064	0.265	0.118	0.45	2.873	18.7	
NaCl	2.060	0.262	0.121	0.46	2.913	17.1	16[b]
CsCl	2.203	0.197	0.030	0.15	2.058	37.1	
AsNi	2.056	0.257	0.116	0.28	2.861	18.1	
$P4_2mc$	2.056	0.265	0.113	0.43	2.869	19.5	
$Amm2$	2.091	0.310	0.115	0.37	2.583	28.8	
$I4_1md$	2.088	0.270	0.115	0.43	2.869	19.8	

[a]Ref. [27], [b]Ref. [28]

4. Conclusions

In summary, according to the above investigation, we draw the conclusions that are listed below.

(i) It is predicted that the tetragonal $P4_2mc$, $I4_1md$, and orthorhombic $Amm2$ phases of VN are energetically more stable than NaCl type structure. Together with WC, CsCl, NaCl, and AsNi phases, it is found that the phase transition from WC to CsCl structure occurs at 256 GPa. Further experimental investigations may be required to clarify the new predicted phases and the WC–CsCl structural phase transition.

(ii) The structural parameters, elastic and thermodynamic properties of VN in considered structures are derived. It is found that the Debye temperatures of $P4_2mc$, $Amm2$, and $I4_1md$ phases are all higher than those of other structures. The hexagonal WC and AsNi type VN are mechanical stable at pressures up to 300 GPa and 250 GPa, respectively. The cubic NaCl type is stable only as pressure increases up to 125 GPa, and the CsCl type VN is stable at pressures above 256 GPa. The predicted three new phases are all stable until pressure increases up to 300 GPa based on the mechanical stable criteria.

(iii) The calculated results of the band structure and density of states of WC type indicate that VN is metallic. The bonding nature of N and V are strongly hybridized as covalence. The calculations on the hardness values of VN in considered structures indicate that the $P4_2mc$, $Amm2$, and $I4_1md$ structures are potential superhard phases.

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