Structure and mechanical properties of tantalum mononitride under high pressure: A first-principles study

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The structure and mechanical properties of tantalum mononitride (TaN) are investigated at high pressure from first-principles using the plane wave pseudopotential method within the local density approximation. Three stable phases were considered, i.e., two hexagonal phases (ϵ and θ) and a cubic δ phase. The obtained equilibrium structure parameters and ground state mechanical properties are in excellent agreement with the experimental and other theoretical results. A full elastic tensor and crystal anisotropy of the ultra-incompressible TaN in three stable phases are determined in the wide pressure range. Results indicated that the elastic properties of TaN in three phases are strongly pressure dependent. And the hexagonal θ -TaN is the most ultraincompressible among the consider phases, which suggests that the θ phase of TaN is a potential candidate structure to be one of the ultraincompressible and hard materials. By the elastic stability criteria, it is predicted that θ -TaN is not stable above 53.9 GPa. In addition, the calculated B/G ratio indicated that the ϵ and δ phases possess brittle nature in the range of pressure from 0 to 100 GPa. While θ phase is brittleness at low pressure (below 8.2 GPa) and is strongly prone to ductility at high pressure (above 8.2 GPa). The calculated elastic anisotropic factors for three phases of TaN suggest that they are elastically highly anisotropic and strongly dependent on the propagation direction.

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I. INTRODUCTION

The transition metal nitrides (TMN), become more and more important series of materials in various industrial applications owing to their outstanding and unique physical properties, such as chemical and thermal stabilities, high hardness and strength, high melting point, good thermal and electronic conductivity, and superconductivity.^{1–3} Especially, 5d-TM dinitrides (PtN_2 , IrN_2 , and OsN_2) have been studied widely and synthesized under high pressure and temperature, showing very high bulk modulus and high shear modulus.^{4–9} However, the drawback of these TMN_2 is their extreme high-pressure condition for synthesizing them. Moreover, theoretical results show that experimental synthesized of 5d-TMN₂ are metastable. On the contrary, 5d-TM tantalum mononitride (e.g., TaN), which different from these metastable 5d TMN₂, it can be synthesized under ambient pressure condition and has three stable phases, i.e., the two hexagonal phases (ϵ -type structure with the space group of P-62m, No:189;¹⁰ θ -type structure with the space group of P-6m2, No:187 (Ref. 11)) and a cubic NaCl phase (δ -type structure with space group of Fm-3m, No:225).¹² In view of its excellent mechanical and thermal properties, it has been widely used in hard wear-resistant coatings, diffusion barriers, optical coatings, cutting tools, magnetic storage devices, generators, and maglev trains, etc.¹³ These wide ranges of interesting applications have lead to much efforts that have been devoted to this fascinating material.^{14–30}

In the past, a number of studies mainly focus on cubic δ phase of TaN by the various methods^{14–19} and also synthesized by diverse methods,^{20–22} calculations show very high bulk modulus (above 328 GPa) and suggest that TaN is in cubic δ phase with high hardness. Compared to the cubic phase, the ϵ and θ phases have not been studied deeply. Recently, in order to search for less compressible transition metal nitrides materials, the calculations have been performed on the other two stable phases of TaN. The experimental results show that the hexagonal ϵ phase is the most stable one at ambient conditions, the hexagonal θ phase is a low temperature high-pressure phase, and cubic δ phase is a high-temperature high-pressure phase.²³ Moreover, the hexagonal θ phase and cubic δ phase have much higher hardness than that of hexagonal ϵ phase.²⁴ Very recently, a few theoretical studies^{25–28} are performed on finding all the possible structures of TaN, which are very important on looking for new superhard materials. Li *et al.*²⁵ and Zhao *et al.*²⁶ investigated the structural, electronic, and mechanical properties of TaN by the first principle calculations. They found that TaN in θ phase is a potential candidate to be ultra-incompressible and hard. The several phase structural stability and electronic properties of TaN are investigated using the density functional theory (DFT) calculations.^{27,28} Results indicated that TaN in θ phase may be a less compressible material. Although there are some studies, still the mechanical properties of TaN under high pressure are limited both experimentally and theoretically as far as we are aware. Especially, the elastic constants and anisotropy under pressure are very important to determine the response of the crystal to external forces, as characterized by the bulk and shear moduli and can provide a deeper insight into mechanical behavior and

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hardness of materials. Moreover, it is essential for many practical applications, such as load deflection, thermoelastic stress, and fracture toughness.²⁹ Therefore, an explicit determination of its elastic properties as a function of pressure is essential, and will have important guidable significances to accelerate the synthesis of TaN.

In this work, we focus on the structure and mechanical properties for three stable phases of TaN to study the pressure dependence of structure and mechanical properties and discuss the application implications of our results. The rest of this paper is structured as follows. In Sec. II, we give a brief description of the theoretical method. The results and some discussions of structural, elastic, and anisotropy of TaN under high pressure are presented in Sec. III. Conclusions derived from our calculations are drawn in the Sec. IV.

II. COMPUTATIONAL METHOD

In this work, the first-principles calculations are performed based on the DFT in CASTEP program.³⁰ Non-local ultrasoft pseudo potential (USPP) introduced by Vanderbilt³¹ was employed for all ion–electron interactions. The exchange–correlation functional is treated within the local density approximation (LDA–CAPZ) proposed by Vosko *et al.*³² Pseudo-atom calculations are performed for Ta: 5d³ 6s² and N: 2s² 2p³. The electronic wave functions are expanded in a plane wave basis set with energy cut-off of 330 eV for hexagonal ϵ and θ phases, 380 eV for cubic δ phase, the Monkhorst-Pack k -point of $3 \times 3 \times 6$ was used for hexagonal ϵ phase, $6 \times 6 \times 6$ for hexagonal θ and cubic δ phase. The convergence was checked with respect to the k -point density and the plane-wave cutoffs. Structures were relaxed using the Broyden, Fletcher, Goldfarb, and Shannon (BFGS) minimization method algorithm.³³ After structural optimization, the residual force is less than 0.01 eV/Å, the max displacement of atoms is less than 5.0×10^{-4} Å, and the convergence threshold for the maximum stress limited to 0.02 GPa. All these parameters were tested to ensure that the self-consistent total energies converged to 5.0×10^{-6} eV/atom.

It is well known that the first principles calculation based on DFT can be used to obtain reliable elastic properties of inorganic compounds. Several methods are available for computation of elastic constants, but currently the stress-strain method seems to be most commonly used, and this is the method used in this work, which has been successfully applied in our previous work.³⁴ The elastic constants C_{ijkl} with respect to the finite strain variables are defined as^{35,36}

$$C_{ij} = \left(\frac{\partial \sigma_{ij}(x)}{\partial e_{kl}} \right)_x, \quad (1)$$

where σ_{ij} and e_{kl} are the applied stress and Eulerian strain tensors, respectively; and X and x are the coordinates before and after the deformation, respectively. For the isotropic stress, we have³⁶

$$C_{ijkl} = c_{ijkl} + \frac{P}{2} (2\delta_{ij}\delta_{kl} - \delta_{il}\delta_{jk} - \delta_{ik}\delta_{jl}), \quad (2)$$

$$c_{ijkl} = \left(\frac{1}{V(x)} \frac{\partial^2 E(x)}{\partial e_{ij} \partial e_{kl}} \right)_x, \quad (3)$$

where c_{ijkl} denote the second-order derivatives with respect to the infinitesimal strain (Eulerian). The fourth-rank tensor C has generally 21 independent components. However, this number is greatly reduced when taking into account the symmetry of the crystal. For the hexagonal crystal, three strain patterns brought out stresses related to all the five independent elastic coefficients, which are usually referred to as C_{11} , C_{33} , C_{44} , C_{12} , and C_{13} . For a cubic crystal, symmetry reduces to three (C_{11} , C_{12} , and C_{44}).

Elastic modulus values can be obtained directly within these elastic constants based on the Voigt-Reuss-Hill method (VRH). For the hexagonal structure of TaN, The formulas as follows:

$$\begin{aligned} B_V &= \frac{1}{9} [2(C_{11} + C_{12}) + C_{33} + 4C_{13}], \\ B_R &= \frac{(C_{11} + C_{12})C_{33} - 2C_{13}^2}{C_{11} + C_{12} + 2C_{33} - 4C_{13}}, \\ B &= \frac{1}{2} (B_V + B_R), \\ G_V &= \frac{1}{30} (C_{11} + C_{12} + 2C_{33} - 4C_{13} + 12C_{44} + 12C_{66}), \\ G_R &= \frac{5}{2} \frac{\left((C_{11} + C_{12})C_{33} - 2C_{13}^2 \right)^2 C_{44} C_{66}}{3B_V C_{44} C_{66} + \left((C_{11} + C_{12})C_{33} - 2C_{13}^2 \right)^2 (C_{44} + C_{66})}, \\ G &= \frac{1}{2} (G_V + G_R), \end{aligned} \quad (4)$$

where

$$C_{66} = \frac{1}{2} (C_{11} - C_{12}). \quad (5)$$

The polycrystalline modulus is the arithmetic mean values of the Voigt and Reuss module

$$B_H = \frac{1}{2} (B_V + B_R), \quad G_H = \frac{1}{2} (G_V + G_R). \quad (6)$$

To prove the mechanical anisotropy of TaN compounds, linear moduli along a axis (B_a) and c axis (B_c) can be defined

$$B_a = a \frac{dP}{da} = \frac{\Lambda}{2 + \alpha}, \quad B_c = c \frac{dP}{dc} = \frac{B_a}{\alpha}, \quad (7)$$

where $\Lambda = 2(C_{11} + C_{12}) + 4C_{13}\alpha + C_{33}\alpha^2$ and $\alpha = \frac{C_{11} + C_{12} - 2C_{13}}{C_{33} - C_{13}}$

For the cubic structure of TaN, the elastic modulus values are obtained

$$\begin{aligned} B_V &= B_R = (C_{11} + 2C_{12})/3, \quad G_V = (C_{11} - C_{12} + 3C_{44})/5, \\ G_R &= 5(C_{11} - C_{12})C_{44}/[4C_{44} + 3(C_{11} - C_{12})]. \end{aligned} \quad (8)$$

In terms of the Voigt-Reuss-Hill approximations, Young's modulus E and Poisson's ratio ν are also obtained by the following formulas:

$$E = 9BG/3B + G, \quad \nu = 3B - 2G/[2(3B + G)]. \quad (9)$$

III. RESULTS AND DISCUSSION

A. Equilibrium structure and ground-state mechanical properties

One method to determine the accuracy of the calculations is to compare the calculated lattice parameters with

those determined experimentally. Therefore, in order to obtain reliable equilibrium structure parameters for the three stoichiometric phases of TaN, we first make the total energy electronic structure calculations by the first-principles method. The ionic configurations and lattice vectors of TaN were fully optimized. The obtained equilibrium lattice parameters and bulk modulus for each phase are compiled in Table I together with the available experimental values and previous theoretical results for comparison. For ϵ phase, the calculated lattice parameters 5.193 and 2.905 Å are in fair agreement with the experimental data.¹⁰ They match each other within 0.1% for a axes and 0.3% for c axes. For θ phase, the calculated lattice parameters 2.915 and 2.868 Å

TABLE I. Calculated equilibrium lattice parameters (in Å), equilibrium volume V (in Å³), elastic constants C_{ij} , bulk modulus B , shear modulus G , Young's modulus E , Poisson's ratio ν , and B/G for TaN.

	Hexagonal ϵ phase			Hexagonal θ phase			Cubic δ phase		
	Present	Theory	Expt.	Present	Theory	Expt.	Present	Theory	Expt.
a	5.193	5.229 ^a , 6.051 ^b , 5.229 ^c , 5.226 ^d	5.196 ^e	2.915	2.947 ^{a,c} , 3.018 ^b , 2.946 ^d	2.936 ^f , 2.934 ^g , 2.938 ^h	4.386	4.415 ^a , 4.547 ^b , 4.42 ^{i,j} , 4.37 ⁱ , 4.33 ^k , 4.40 ^l , 4.41 ^m , 4.414 ^{c,d}	4.331 ⁿ , 4.332 ^o , 4.336 ^p , 4.427 ^q
c	2.905	2.919 ^a , 2.989 ^b , 2.918 ^c , 2.920 ^d	2.911 ^e	2.868	2.896 ^{a,c} , 2.967 ^b , 2.897 ^d	2.885 ^f , 2.880 ^g , 2.868 ^h			
V	67.84	69.12 ^a , 94.78 ^b , 69.09 ^c , 69.06 ^d	68.06 ^e	21.10	21.8 ^{a,c} , 23.4 ^b , 21.8 ^d	21.54 ^f , 21.47 ^g	21.09	21.5 ^{a,c} , 21.0 ^b	20.31 ⁿ , 21.69 ^q
C_{11}	539.9	538 ^a , 472 ^b , 535 ^c		610.8	616 ^a , 556 ^b , 640 ^c		898.4	817 ^a , 678 ^b , 783 ^r , 675.95 ^l , 772 ^c	
C_{33}	711.7	665 ^a , 726 ^b , 673 ^c		883.7	818 ^a , 737 ^b , 822 ^c				
C_{44}	221.4	191 ^a , 243 ^b , 193 ^c		294.5	256 ^a , 222 ^b , 244 ^c		63.8	71 ^a , 46 ^b , 65 ^c , 266.92 ^l , 20 ^r	
C_{12}	275.5	238 ^a , 270 ^b , 218 ^c		341.0	212 ^a , 205 ^b , 217 ^c		130.7	112 ^a , 119 ^b , 132 ^c , 154.48 ^l , 167 ^r	
C_{13}	205.1	165 ^a , 145 ^b , 179 ^c		183.7	142 ^a , 152 ^b , 162 ^c				
B	348	319 ^a , 310 ^b , 320 ^c		378	337 ^a , 318 ^b , 354 ^c		389	347 ^a , 306 ^b , 328.3 ^j , 403.85 ^k , 329 ^m , 372 ^r , 349 ^c	
G	182	182 ^a , 191 ^b , 197 ^c		220.4	243 ^a , 213 ^b , 268 ^c		143.8	144 ^{a,c} , 139 ^b	
E	466	458 ^a , 669 ^b , 491 ^c		553.5	588 ^a , 676 ^b , 642 ^c		383.8	380 ^a , 642 ^b , 379 ^c	
ν	0.246	0.26 ^a , 0.196 ^b , 0.25 ^c		0.256	0.21 ^a , 0.2 ^c , 0.199 ^b		0.335	0.32 ^a , 0.150 ^b , 0.32 ^c	
B/G	1.91	1.753 ^a , 1.62 ^b , 1.624 ^c		1.715	1.39 ^a , 1.49 ^b		2.689	2.41 ^a , 2.20 ^b	

^aReference 26. VASP PAW+GGA.

^bReference 25. Vanderbilt ultrasoft pseudopotential and GGA.

^cReference 28. VASP PAW+GGA.

^dReference 23. VASP pseudopotential and GGA.

^eReference 10. Expt.

^fReference 37. plane-wave pseudopotential method within LDA.

^gReference 24. Expt.

^hReference 11. Expt.

ⁱReference 15. FLAPW+GGA.

^jReference 16. FP-LAPW + lo method within LDA.

^kReference 14. KKR method within X_a exchange approximation.

^lReference 27. ESPRESSO+GGA

^mReference 19. US-PP within GGA.

ⁿReference 20. Expt.

^oReference 22. Expt.

^pReference 21. Expt.

^qReference 13. Expt.

^rReference 17. ABINIT DFT+LDA

are also in good agreement with the experimental results.^{11,24,37} Their difference is within 0.8% and 0.6% for a and c axes, respectively. For δ phase, the mismatch of lattice parameter is within 0.9% compared with experimental values.^{13,20-22} From above, it is clear that the agreement of our calculation with experiment and other theoretical values is seen to be quite good. The good agreements show that the choice of pseudopotential and approximation is reasonable for the current study and our present calculations are reliable.

In Table I, we also listed the calculated bulk modulus of TaN, it is obvious that the bulk moduli of θ phase (378 GPa) are higher than those of the ε and δ phases, and also higher than those of the synthesized ultra-incompressible materials, such as ReB₂ of 354 GPa,³⁸ OsN₂ of 359 GPa,³⁹ IrN₂ of 327 GPa,⁴⁰ and PtN₂ of 272 GPa,⁴¹ which suggests that θ -TaN is possessing ultra-incompressible and hard characteristic. In addition, it is now well recognized that shear modulus is regarded as a better indicator for hardness than bulk modulus.^{42,43} A large shear modulus implies a larger hardness of materials. Thus, from Table I we can see that θ -TaN has the largest shear modulus, is 220.4 GPa, than in ε -TaN (182 GPa) and δ -TaN (143.8 GPa), which suggests that the θ -TaN has the largest hardness among the considered phases and agreement with the recent theoretical studies.^{24,27} It also suggests that θ -TaN is a potential candidate structure to be one of the ultraincompressible and hard materials.

Further to check our conjecture, the pressure dependence of the normalized parameters a/a_0 , c/c_0 , and volume V/V_0 as a function of pressure is exhibited in Figures 1 and 2. The curves (Figure 1) present the compressibility of TaN in ε , θ , and δ phases are smaller along the c axis than those along a axis. The normalized parameters a/a_0 in δ phase are slightly larger than those in ε and θ phases, which indicates that the δ -TaN has the largest incompressibility in a axis direction among the considered phases. It can be also found that the ε phase is the most easily compressed in a and c axis directions as compared to the other two phases. In addition, from the normalized volumes V/V_0 (Figure 2), it is not difficult to find that the incompression curve is nearly identical and indistinguishable in θ and δ phases of TaN and much more

FIG. 1. The normalized parameters a/a_0 and c/c_0 as a function of pressure for ε , θ , and δ phases in TaN.

FIG. 2. The normalized parameter V/V_0 as a function of pressure for ε , θ , and δ phases in TaN.

incompressible than that in ε phase. Therefore, the above results also provide a clear signal that the TaN in θ phase is very low compressibility, which makes it become the potential stuff of superhard materials. We expect that they can also be synthesized under certain extreme conditions in the future.

B. Elastic properties

The predicted zero pressure elastic stiffness coefficients (C_{ij}), five for the hexagonal phase (C_{11} , C_{33} , C_{44} , C_{12} , and C_{13}) and three (C_{11} , C_{44} , and C_{12}) for the cubic phases of TaN, are determined using stress-strain relation derived from the method described above. These results are also listed in Table I. Generally, the error in elasticity calculations based on the DFT is order of 10%, resulted mainly from the exchange-correlation approximation and the pseudopotential employed in the calculations. From Table I, our results are in reasonable agreement with those obtained by the projector augmented-wave (PAW) method,^{26,28} the DFT method,²⁵ the FLAPW plus local orbitals (FLAPW + lo) method,¹⁶ the relativistic Korringa, Kohn, and Rostoker (KKR) method,¹⁴ and the density functional perturbation theory (DFPT) method.¹⁷ Thus, consider the typical error, the good agreement between current and previous results, supporting the accuracy and reliability of our elastic calculations.

As is known to all, the requirement of mechanical stability in a hexagonal crystal leads to the following restrictions on the elastic constants: $C_{11} > C_{12}$, $C_{44} > 0$, and $(C_{11} + 2C_{12})C_{33} > 2C_{13}^2$. For cubic crystals, the three generally accepted mechanical stability can be judged from the following criteria: $C_{11} + 2C_{12} > 0$, $C_{44} > 0$, and $C_{11} - C_{12} > 0$. Obviously, from the calculated values of C_{ij} in Table I, the above restrictions are all satisfied for these three phases of TaN, implying that the three phases of TaN are mechanically stable at ambient condition. In addition, one should be aware that the values presented in Table I were obtained at $P=0$ GPa, and that pressure effects will generally increase the elastic constants.

Therefore, we expect the experimental data for TaN at ambient condition to be smaller than those listed here.

From Table I, it is also seen that the calculated C_{33} of hexagonal θ phase of TaN (898 GPa) is larger than c -BN of 818 GPa,⁴⁴ smaller than diamond of 1106 GPa.⁴⁴ The large C_{33} which measures the c -direction resistance to linear compression can be mainly attributed to the N atoms along the c -direction. It is corresponding with the above determined that θ phase is much more difficult compressed in c -axis direction than ε phase.

The elastic constants of three phases of TaN varying with pressure are shown in Figure 3. Unfortunately, to the best of our knowledge, there are not yet experimental data or theoretical calculation to compare with our predicted results for the pressure derivative of elastic properties of TaN in these three phases. Therefore, we believe that, our results can serve as a prediction for future investigations. Generally speaking, the diagonal elements C_{ii} describe the crystal stiffness under uniaxial compression and shear, while the off-diagonal elements $C_{ij}(i \neq j)$ correspond to biaxial compression and distortion of the crystal. From Figure 3, we found that there is remarkable anisotropy in the diagonal elements C_{ii} ($i = 1, 3, 4$) of the elastic constant tensor, which can be related to the crystal structure. Thus, for TaN it can be concluded that it is anisotropic upon compression in this three phases. In addition, the elastic constants C_{ij} of these phases increase monotonously with pressure except the C_{44} of cubic δ phase that decreases, which suggests that the anisotropy of TaN is weakened with increasing pressure slightly. Especially, for the cubic δ phase, it is found that C_{11} varies largely under the effect of pressure as compared with the variations in C_{12} and C_{44} . The elastic constant C_{11} represents elasticity in length, longitudinal strain which produces a change in C_{11} . The elastic constants C_{12} and C_{44} are related to the elasticity in shape. A transverse strain causes a change in shape without a change in volume. Therefore, C_{12} and C_{44} are less sensitive to pressure as compared with C_{11} .

For hexagonal crystal, the mechanical stability leads to restrictions on the elastic constants under isotropic pressure as follows:⁴⁵

FIG. 3. Pressure dependence of the elastic stiffness coefficients (C_{ij}) of TaN in ε , θ , and δ phases at 0 K.

FIG. 4. The relations between the C_{44} - P and the pressures of TaN in ε , θ , and δ phases.

$$\begin{aligned} \tilde{c}_{44} &> 0, \quad \tilde{c}_{11} > |\tilde{c}_{12}|, \\ (\tilde{c}_{22} + \tilde{c}_{33} - 2\tilde{c}_{23}) &> 0, \quad \tilde{c}_{33}(\tilde{c}_{11} + \tilde{c}_{22}) > 2\tilde{c}_{13}, \end{aligned} \quad (10)$$

where $\tilde{c}_{\alpha\alpha} = C_{\alpha\alpha} - P$ ($\alpha = 1, 3, 4$), $\tilde{c}_{12} = C_{12} + P$, and $\tilde{c}_{13} = C_{13} + P$.

Figure 4 shows $\tilde{c}_{44}$ versus pressures for TaN. When $\tilde{c}_{44} > 0$, it is no longer fulfilled, indicating that the θ phase of TaN is not mechanical stable at pressures about 53.9 GPa.

To further probe into the physical properties of these three phases in TaN, we analyzed their ductility and brittle nature under pressure according to the Pugh criterion.⁴⁶ Bulk modulus B is a factor that indicates the resistance to volume change by applied pressure, while the shear modulus G represents the resistance to plastic deformation. A high B/G ratio is associated with ductility, whereas a low value corresponds to brittle nature. If $B/G > 1.75$, the material behaves in a ductile manner; otherwise, the material behaves in a brittle manner. Thus, in this work, the relations between B/G ratio and pressure for TaN in three phases are exhibited in Figure 5.

FIG. 5. The relations between B/G ratio and pressure for TaN in ε , θ , and δ phases.

It is obvious that the ratio of B/G in the three phases increases with pressure. Obviously, for ε and δ phases, the B/G ratios are greater than 1.75 at 0 GPa, which indicated that the ε and δ phases possess brittle nature at 0 GPa. This is in agreement with the Refs. 25 and 26. While the ration of B/G in θ phase is less than 1.75 under low pressure (around 8.2 GPa). The results indicated that θ -TaN is prone to brittleness at low pressure (below 8.2 GPa) which similar to the superhard material c -BN, and is strongly prone to ductility at high pressure (above 8.2 GPa).

C. Elastic anisotropy

It is well known that microcracks are easily induced in the materials due to significant elastic anisotropy.⁴⁷ Especially, for the hard materials, it should preferably be isotropic; otherwise, it would deform preferentially in a given direction. That is to say, microcracks may be induced in materials owing to elastic anisotropy. Therefore, a proper

analysis of elastic anisotropic behavior can provide a deeper insight into mechanical behavior and hardness of materials. Table II lists the all isotropic moduli of ε -, θ -, δ -TaN under different pressures, i.e., bulk modulus B , shear modulus G , Young's modulus E , compressibility K , and Poisson's ratio ν . Using Eq. (7), we predicted the linear moduli along the a -axis and b -axis given by B_a and B_c , respectively. It is shown in Table II. From our calculations, it is clear that with the pressure increasing, the B_a and B_c of two hexagonal phases generally increase. It is indicated that both phases are all elastic anisotropic. That B_a smaller than B_c reveals that the compression along a -axis is more easier than that along c -axis in the two hexagonal phases, which is consistent with the pressure dependence of the normalized parameters a/a_0 and c/c_0 . This phenomenon can be understood by the knowledge of the bonding situations in TaN, which are characterized as the strong chemical bonding between the Ta and the N atoms. When pressure increases, the atoms in the TaN compound become closer, and their interactions become

TABLE II. The calculated elastic modulus for ε , θ , and δ phases of TaN under pressure.

P (GPa)	Bulk modulus, B (GPa)	Shear modulus, G (GPa)	Young's modulus, E (GPa)	Compressibility K (1/GPa)	Poisson's ratio ν	B_a (GPa)	B_c (GPa)
<i>Hexagonal ε phase</i>							
0	349.83	182.3	465.96	0.0029	0.246	977.68	1224.52
10	398.19	196.02	505.17	0.0025	0.288	1114.37	1390.36
20	442.32	207.09	537.40	0.0023	0.274	1227.50	1579.42
30	483.24	216.60	565.33	0.0021	0.305	1350.98	1690.20
40	530.02	223.40	587.64	0.0019	0.293	1459.26	1931.57
50	574.01	229.97	608.63	0.0017	0.324	1582.60	2084.49
60	613.03	234.26	623.38	0.0016	0.313	1647.28	2389.83
70	648.86	244.60	651.89	0.0015	0.333	1692.42	2772.07
80	696.67	261.21	696.57	0.0014	0.316	1879.29	2689.78
90	734.64	276.65	737.39	0.0014	0.333	1967.68	2892.15
100	774.63	283.43	757.86	0.0013	0.337	2065.86	3092.13
<i>Hexagonal θ phase</i>							
0	378.35	220.36	553.60	0.0026	0.256	1104.25	1325.85
10	446.61	238.24	606.82	0.0023	0.2736	1223.64	1489.98
20	487.35	269.45	682.55	0.0021	0.2666	1347.86	1632.05
30	543.66	267.91	690.33	0.0019	0.2886	1470.37	1909.68
40	569.98	281.88	725.97	0.0018	0.288	1587.21	2020.09
50	615.80	289.23	750.23	0.0016	0.297	1702.06	2217.76
60	660.88	299.79	781.24	0.0015	0.303	1815.65	2421.71
70	690.53	324.82	842.38	0.0015	0.297	1929.45	2440.99
80	746.09	321.09	842.42	0.0013	0.312	2038.37	2779.34
90	776.46	347.91	908.10	0.0013	0.305	2153.92	2773.95
100	818.83	339.69	895.27	0.0012	0.318	2262.85	2954.59
<i>Cubic δ phase</i>							
0	386.61	143.78	383.77	0.0026	0.335		
10	432.88	152.65	409.78	0.0023	0.3425		
20	480.77	161.16	434.89	0.0021	0.3495		
30	526.79	168.09	455.79	0.0019	0.356		
40	570.29	174.41	474.83	0.0018	0.361		
50	615.03	181.50	495.74	0.0016	0.366		
60	653.53	186.70	511.40	0.0015	0.370		
70	697.55	191.92	527.39	0.0014	0.374		
80	745.35	197.06	543.30	0.0013	0.379		
90	788.60	201.77	557.74	0.0013	0.382		
100	828.98	205.92	570.52	0.0012	0.385		

TABLE III. Anisotropy factors ΔP , ΔS_1 , and ΔS_2 for three phases of TaN under pressure.

P (GPa)	Hexagonal ε phase			Hexagonal θ phase			Cubic δ phase		
	ΔP	ΔS_1	ΔS_2	ΔP	ΔS_1	ΔS_2	A	ΔS_1	ΔS_2
0	1.3191	0.9502	1.6742	1.4492	0.9575	2.1859	-0.7125	6.0160	0.1662
10	1.3005	0.9136	1.7357	1.4664	0.9565	2.2518	-0.7314	6.8815	0.1453
20	1.3076	0.8675	1.8472	1.3965	0.9364	1.9984	-0.7446	7.7647	0.1288
30	1.2835	0.8267	1.9524	1.4692	0.8896	2.3798	-0.7573	8.8260	0.1133
40	1.3008	0.7825	2.0952	1.4459	0.8663	2.4438	-0.7696	10.0321	0.0997
50	1.2577	0.7113	2.1788	1.4594	0.8392	2.6215	-0.7775	11.1444	0.0897
60	1.2641	0.6501	2.2895	1.4648	0.8165	2.7251	-0.7885	12.6368	0.0791
70	1.2765	0.6148	2.2857	1.4101	0.8211	2.5200	-0.7953	14.2959	0.0700
80	1.2394	0.6393	2.2442	1.4578	0.7776	2.8844	-0.7991	16.1357	0.0620
90	1.2788	0.6714	2.2737	1.3969	0.7792	2.6297	-0.8045	18.3316	0.0546
100	1.2794	0.6524	2.3546	1.4282	0.7505	3.0791	-0.8105	21.0408	0.0475

stronger that play an important role to form a superhard material. These mechanical properties also imply the anisotropy of TaN.

In addition, for the hexagonal phase, the anisotropy of compressional wave is obtained from $\Delta P = C_{33}/C_{11}$, the anisotropies of the wave polarized perpendicular to the basal plane (S_1) and the polarized basal plane (S_2) are calculated as

$$\Delta_{S1} = \frac{C_{11} + C_{33} - 2C_{13}}{4C_{44}}, \quad \Delta_{S2} = \frac{2C_{44}}{C_{11} - C_{12}}. \quad (11)$$

The relations of calculated three type anisotropies of elastic waves ΔP , Δ_{S1} , and Δ_{S2} dependences on pressures for the two hexagonal phases are listed in Table III. It can be observed that ΔP and Δ_{S1} show decreasing trend with increasing pressures, in which Δ_{S2} increases rapidly with pressures but ΔP and Δ_{S1} are relatively moderate. Both the compressional wave (P) and shear wave velocities (S) are found to be strongly dependent on the propagation direction, suggesting that hexagonal phase of TaN is elastically highly anisotropic in the pressure range of 0 to 100 GPa.

For cubic phase of TaN, Δ_{S1} and Δ_{S2} can be obtained as follows:

$$\Delta_{S1} = \frac{1}{\Delta_{S2}} = \frac{C_{11} - C_{12}}{2C_{44}}. \quad (12)$$

The calculated Δ_{S1} and Δ_{S2} and anisotropic factors $A = (2C_{44} + C_{12})/C_{11}$ are also listed in Table III. It is obvious that cubic TaN is anisotropic under pressure. Because a value of 1 represents completely elastic isotropy, while values smaller or greater than 1 measure the degree of elastic anisotropy. In addition, the Δ_{S1} generally increases as pressure descends from 0 to 100 GPa. This reveals that the anisotropy will weaken as the pressure increases.

IV. CONCLUSIONS

Three synthesized stable phases for TaN are studied and analyzed under high pressures by the first-principles calculations. Good agreement is obtained with the experimental and other theoretical studies. An analysis of the calculated results

shows that the hexagonal θ phase of TaN possesses the largest shear modulus among the three phases, and also higher than those of the synthesized ultra-incompressible materials, such as ReB₂, OsN₂, IrN₂, and PtN₂. The superior mechanical properties indicate that the hexagonal θ phase is an ultra-incompressible and hard material among the consider phases, the order of hardness of TaN from high to low is: $\theta < \delta < \varepsilon$. It is suggesting that the θ -TaN is a potential candidate structure to be one of the ultraincompressible and hard materials. By the elastic stability criteria, it is predicted that θ -TaN is not stable above 53.9 GPa. In addition, the calculated B/G ratio indicated that the ε and δ phases possess brittle nature at 0 GPa. However, θ phase is prone to brittleness at low pressure and is strongly prone to ductility at high pressure. The calculated elastic anisotropic factors for three phases of TaN suggest that they are elastically highly anisotropic and strongly dependent on the propagation direction. We wish our study could stimulate future experimental study on synthesizing this technologically important ultra-incompressible material.

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