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First-principles investigation of technetium carbides and nitrides

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Phase stabilities and mechanical properties of ideal stoichiometric technetium monocarbide (TcC) and technetium mononitride (TcN) in the tungsten carbide (WC), nickel arsenide (NiAs), rocksalt (NaCl), and zinc-blende (ZnS) structures, respectively, have been studied systematically by first-principles calculations. It is found that both TcC and TcN in two hexagonal phases (WC and NiAs) are not only elastically stable but also hard and ultrastiff materials. Remarkably, for the two hexagonal TcC phases, both bulk moduli and linear incompressibilities along the *c* axis exceed that of *c* BN and even rival with diamond. Their hardness can also match the known hard materials such as WC. The combination of good metallicity, strong stiffness, and high hardness suggests that the materials may find applications as hard conductors and cutting tools.

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I. INTRODUCTION

Ultrahard and superhard materials are of considerable fundamental interest and practical importance because of their excellent mechanical and thermal properties, such as great hardness, large strength, high melting point, and wear resistance. Diamond and *c* BN are superhard materials. However, diamond reacts with iron at moderately high temperature and *c* BN is quite expensive due to its harsh synthesis conditions. These limitations prevent them from being used as abrasives or cutting tools for ferrous metals. Hence, a lot of effort[1–16] has been devoted to finding new hard materials in place of diamond, although the design of superhard materials (hardness$>$40 GPa) is still a huge challenge to scientists. The intercalation of small covalent atoms (B, C, N, and O) into transition metals is a well-known strategy for designing hard materials.[1,9,17] Consequently, the recent discovery of the low compressibility of osmium, revealed by Cynn *et al.*,[18] gave a new interest to borides, carbides, nitrides, oxides, and their high-pressure phases of transition metals. A primary example and among the first synthesized materials following this principle is OsB_2,[2,3] which was expected to be an ultraincompressible hard material. However, further calculations[4–7] indicate that OsB_2 was only a harder material and not a superhard material. Moreover, the ideal shear strength of OsB_2 was just 9.1 GPa due to the weak Os-Os metallic bonding layers.[8] Although Kempter and Nadler[12] claimed to have synthesized WC-structured OsC at ambient pressure and high temperature many years ago, its crystal structure has been disputed and no prominent hardness has yet been found in several phases.[13–16] Fortunately, OsN_2 has been successfully synthesized, but the exact structures is still not well resolved.[19]

In order to hunt for new hard materials, researchers start to look closely at other transition-metal elements surrounding Os in the periodic table. Experimentally, Chung *et al.*[9] successfully synthesized ReB_2 and reported that it is an ultraincompressible superhard material with an average hardness of 48 GPa. To our surprise, several platinum-metal nitrides PMN_2 [PM=Os, Ir, Pt, and Pd (Refs. 19 and 20)] have now been synthesized primarily under conditions of high pressure and temperature (in the range of 60 GPa and 2000 K, respectively) since heavy transition metals were not previously known to form nitrides with high nitrogen content. Also, PtC has been synthesized by Ono *et al.*[21] Theoretically, both the thermodynamic stabilities of six platinum-metal nitrides PMN_2 [PM=Ru, Rh, Pd, Os, Ir, and Pt (Ref. 22)] and the mechanical stabilities of the eight noble-metal carbides NMC [NM=Ru, Rh, Pd, Ag, Os, Ir, Pt, and Au (Ref. 23)] have been systematically studied using density-functional theory. Very recently, Chen *et al.*[24] computationally designed ReC in the WC and NiAs structures with very high bulk and shear modulus and claimed that these two types of ReC phases may be the hardest binary metal carbides so far discovered. Nevertheless, the existence of ReC in the WC or NiAs structure has not been confirmed in experiment.

Tc lies to the top left of Os in the periodic table, which should have a low compressibility, so it is worth studying mechanical properties of its carbide and nitride. The only existing theoretical report addressing the elastic properties of hypothetical WC-, FeSi-, and OsSi-type TcC was made by Wang.[25] A few experimental studies have been devoted to the synthesis of technetium carbide and nitride. In 1962, Trzebiatowski and Rudzinski[26] first synthesized Tc carbide and claimed that Tc carbide forms the hexagonal structure with 1 wt % C and the fcc structure with 1.4–9 wt % C. Nevertheless, Giorgi and Szklarz[27] reported that Tc carbide was completely resolved as a bcc phase by an x-ray diffraction pattern, although its lattice parameter of 3.985 ± 0.002 Å is in agreement with that of the above fcc structure (3.982 Å). The synthesis of Tc-C has been also realized by German *et al.*[28] in high-temperature vacuum furnace. According to German *et al.*,[28] the structure of Tc-C system also depends on the carbon content and the temperature of preparation, and cubic fcc and orthorhombic structures have been obtained. Moreover, the fcc Tc carbide phase is defective in carbon and a range of Tc:C atomic ratio is from 1:1 to 5:1. For Tc nitride, Trzebiatowski and Rudzinski[29] suggested that at 900–1100 °C a cubic fcc phase was detected with a lattice constant varying from 3.980 to 3.985 Å, according to nitrogen content, and that the maximum nitrogen content approximated to the composition $TcN_{0.76}$. Schwochau[30] reviewed some Tc compounds and the corresponding radiopharmaceutical applications. These experimental works have provided useful information for the understanding of the synthesis and structure of Tc carbide and nitride. The carbide and nitride not only exhibit over a wide range of substoichiometry but they can also form a variety of polytype structures. However, because of the technical difficulties and the radioactive nature of the technetium, it has been very difficult to accurately determine the actual stoichiometry of the carbide and nitride and also the exact position of carbon has not been definitively determined. It is thus of theoretical and experimental importance to solve these issues.

In this work, we have employed the first-principles technique to explore the structural stabilities and mechanical properties of the stoichiometric Tc monocarbide (TcC) and Tc mononitride (TcN). Our results indicate that TcC and TcN in the WC and NiAs structures are mechanically stable. In particular, the bulk moduli of the two hexagonal phases of TcC exceed those of *c* BN and even rival to those of diamond, suggesting that they might be potential ultrastiff and hard materials.

II. CALCULATION METHODS

As we know, most of the transition-metal monocarbides and mononitrides usually crystallize in the cubic NaCl structure (space group $Fm3m$),[31] whereas WC is stable in the hexagonal WC-type structure (space group $P\bar{6}m2$) at room temperature.[32] In addition, the cubic ZnS structure (space group $F\bar{4}3m$) and the hexagonal NiAs structure (space group $P6_3mc$) have previously been reported as possible stable phases of several transition-metal monocarbides and mononitrides.[24] Therefore, four possible structures—namely, WC, NiAs, NaCl, and ZnS types—are chosen for TcC and TcN, respectively.

Our first-principles calculations on TcC and TcN are performed by the BSTATE code[33] using the plane-wave pseudopotential method and employing the local-density approximation (LDA).[34] The ultrasoft pseudopotentials of Vanderbilt[35] are used for the transition-metal Tc and nonmetal C and N elements. Integrations in the Brillouin zone are performed using the Monkhorst-Pack[36] k points generated with $14\times14\times14$, $14\times14\times8$, $14\times14\times14$, and $14\times14\times14$ mesh parameters grid for WC, NiAs, NaCl, and ZnS structures, respectively. The cutoff energy of 30.25 Ry for the plane-wave expansion is used for all the systems. The calculated lattice constants, bulk modulus, and its first pressure derivative are estimated through a least-squares fit of calculated total energy versus volume to the third-order Birch-Burnaghan equation of states (EOS).[37] For the hexagonal systems, structure (c/a ratio) optimizations are performed for each fixed volume. The elastic constants are obtained through our previous methods, which have been demonstrated to be very good in providing accurate and reliable predictions of mechanical properties of transition-metal compounds system.[10,38] The shear modulus, Young's modulus, and Poisson's ratio are calculated according to the Voight-Reuss-Hill bounds.[39]

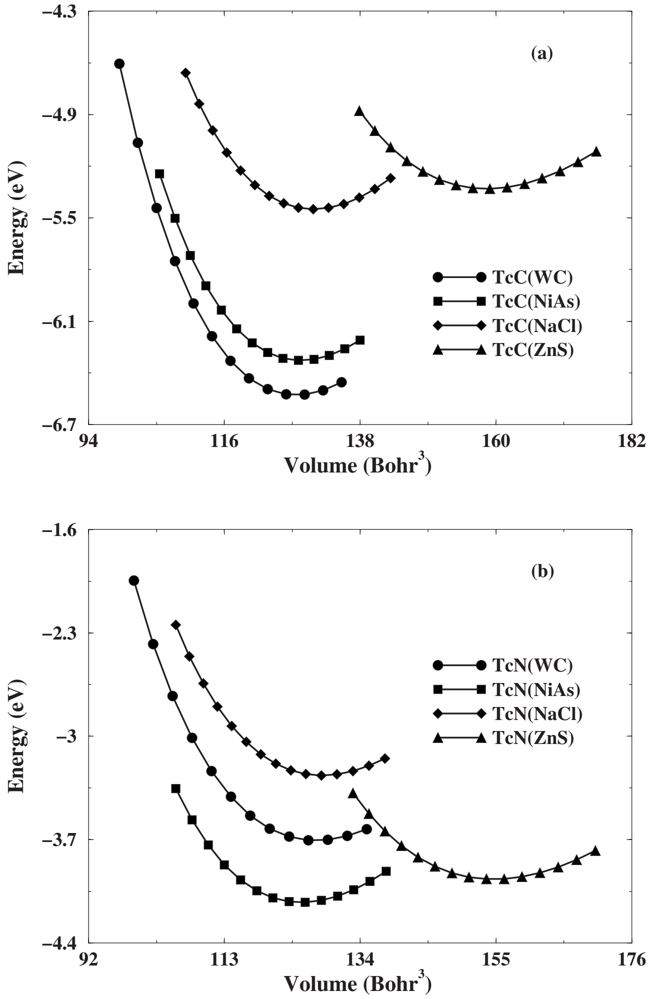

FIG. 1. Calculated total energy versus f.u. volume for the different phases of (a) TcC and (b) TcN.

III. RESULTS AND DISCUSSIONS

Figures 1(a) and 1(b) present the dependences of the calculated total energy on the f.u. volume for the four possible structures—WC, NiAs, NaCl, and ZnS—of TcC and TcN compounds, respectively. For TcC, as shown in Fig. 1(a), two hexagonal structures (WC and NiAs) are energetically far more stable than two cubic phases (NaCl and ZnS). The WC structure is the most energetically favorable phase, whereas the ZnS type is the most unfavorable polymorph with the largest equilibrium volume. For TcN, we observed from Fig. 1(b) that the NiAs type becomes the most stable in energy and the ZnS phase becomes more favorable with respect to the WC and NaCl structures. Besides the relative energy stability above, the mechanical stability of the four possible structures for TcC and TcN will be addressed in the following.

TABLE I. Calculated equilibrium lattice parameters a (Å), axial ratio c/a, bulk modulus B_0 (GPa), its pressure derivative (B_0'), zero-pressure elastic constants C_{ij} (GPa), shear modulus G (GPa), Young's modulus E (GPa), and Poisson's ratio υ for TcC and TcN in the WC, NiAs, NaCl, and ZnS structures compared with our previous data for c BN and diamond (Ref. [10]).

	TcC				TcN					
	WC	NiAs	NaCl	ZnS	WC	NiAs	NaCl	ZnS	c BN	Diamond
a	2.819	2.818	4.260	4.546	2.779	2.762	4.234	4.509	3.590	3.532
c/a	0.974	1.963			1.014	2.029				
B_0	416	405	382	285	385	399	385	312	402	469
B_0'	4.25	4.33	4.39	4.21	4.52	4.75	4.57	4.39	3.62	3.59
C_{11}	752	738	686	299	554	638	660	324	818	1106
C_{33}	1030	966			639	659				
C_{12}	228	187	230	273	224	163	270	305	194	151
C_{13}	199	227			263	383				
C_{44}	198	288	−61	130	31	238	−178	177	479	604
G	252	290		56	86	196		66	403	550
E	629	704		158	240	506		185	907	1186
ν	0.249	0.214		0.407	0.389	0.294		0.401	0.124	0.079

Table I lists the calculated EOS (equilibrium lattice constants, bulk modulus, and its first pressure derivative), elastic constants, shear moduli, Young's moduli, and Poisson's ratios for TcC and TcN in the WC, NiAs, NaCl, and ZnS structures, respectively, at zero pressure and zero temperature. Our previous results for c BN and diamond[10] are also presented for comparison. For the results of WC-type TcC, there is good agreement with the recent work from Wang,[25] indicating that our calculations are reliable. The mechanical stability of any crystal requires the strain energy to be positive, which implies that the whole set of elastic constant C_{ij} satisfies Born-Huang criterion.[40] All the calculated elastic constants C_{ij} have been checked. It is found that the TcC and TcN in the WC and NiAs types are mechanically stable. Nevertheless, for TcC and TcN in the NaCl phase, because negative C_{44} (−61 and −178 GPa) will violate the requirement of positive strain energy, they are elastically unstable in contrast to the experimental observations of cubic NaCl phase.[26,28] There are two possible origins of this disagreement. Our calculation assumes stoichiometric TcC and TcN, while real samples contain C or N deficiency. Another possibility is the effect of temperature. First-principles calculations are valid at zero temperature, while the experimental observations take place at high temperature (above 500 °C). In fact, the influence of vacancy and temperature on the stability of different molybdenum carbide phases by Hugosson *et al.*[41] has confirmed these two factors. Although TcC and TcN in the ZnS structure show elastic stability, smaller bulk moduli (285 and 312 GPa), lower shear moduli (56 and 66 GPa), and larger Poisson's ratios (0.407 and 0.401) imply that their mechanical characters are inferior compared with other phases. Moreover, the electronic structure of TcC in ZnS type displays a weak stability because of large density of states (DOS) in the Fermi level (not shown). Hence, we focus attention on the mechanical properties of the TcC and TcN in two hexagonal structures (WC and NiAs).

From Table I, our bulk moduli of TcC in hexagonal WC and NiAs structures are 416 and 405 GPa, respectively, which are greater than the value of 402 GPa of c BN and even rival with that (469 GPa) of diamond. The elastic constants C_{11} or C_{33} measure the a- or c-direction resistance to linear compression, respectively. We find that C_{11} of TcC in the WC and NiAs phases (752 and 738 GPa) are comparable to that of c BN (818 GPa), while C_{33} (1030 and 966 GPa) exceed C_{11} of c BN and close to C_{11} of diamond (1106 GPa). At the same time, TcC in the WC and NiAs phases also possesses high shear moduli (252 and 290 GPa), large elastic constants C_{44} (198 and 288 GPa), and small Poisson's ratio (0.249 and 0.214), indicating that two hexagonal TcC phases have very strong rigidity against the shear deformations involved in microhardness indentation experiments. For TcN, the bulk moduli in hexagonal WC and NiAs structures have been calculated to be 385 and 399 GPa, respectively, which are slightly smaller than the counterparts of TcC. However, the values of shear modulus and elastic constant C_{44} sharply decrease to 86 and 31 GPa for TcN of the WC structure. The shear modulus (196 GPa) and elastic constant C_{44} (238 GPa) of TcN in the NiAs phase are smaller by 32% and 17%, respectively, compared with the same structure of TcC. To further compare the compressibility of TcC, TcN, diamond, and c BN under pressure, the volume compressions as a function of pressure are displayed in Fig. 2. We clearly notice that TcC in two hexagonal structures is less compressible than c BN, even rivals with diamond. Two hexagonal phases of TcN are marginally more compressible than c BN, but the ZnS phases of TcC and TcN are easily compressed compared with other phases.

It is now well recognized, however, that large bulk and shear moduli do not guarantee high hardness of a material, and thus a quantitative estimate from the semiempirical theory[42,43] is necessary. The theoretical hardness of TcC in the WC and NiAs structures is obtained to be 26 and 25 GPa, respectively, which match hard materials of Al_2O_3 (20.6 GPa) and WC (26.4 GPa).[42] Therefore the present calculations show that two hexagonal TcC phases are ultrastiff and hard materials. The hardness of TcN in the WC and NiAs

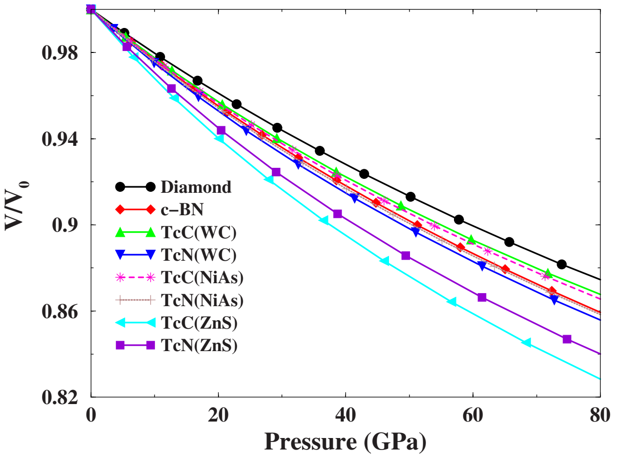

FIG. 2. (Color online) Calculated volume compressions as a function of pressure for TcC, TcN, *c* BN, and diamond.

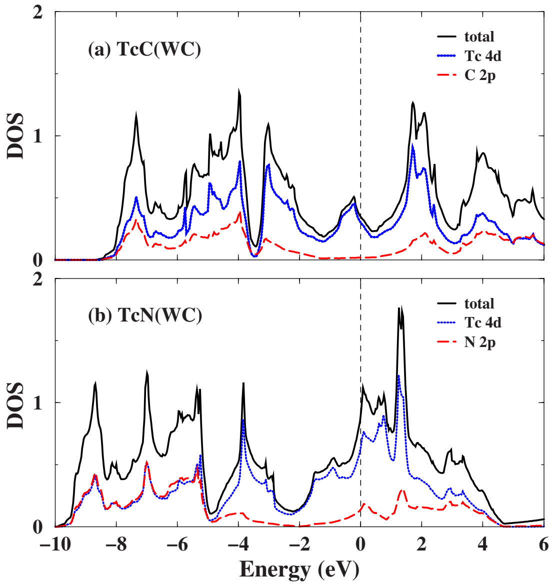

FIG. 3. (Color online) Total and partial DOSs of (a) TcC and (b) TcN in the WC structure. The Fermi level is indicated by a vertical dashed line.

structures has been estimated to be 28 and 29 GPa, respectively. We find that two hexagonal TcN phases are more compressible than the corresponding TcC phases, but their hardness is slightly enhanced, which further indicates that the dependence of hardness on incompressibility is not unequivocal or monotonic. In contrast with our predicted hardness of TcC, the measured values of the samples are in the range of 2.2–4.7 GPa.[28] Such large discrepancy between the theory and the experiment may come from many aspects, but composition, temperature, and structure are three main factors. Our estimated hardness is based on hexagonal stoichiometric TcC at ambient condition, while the measured samples are a mixture of cubic Tc$_x$C ($2<x<6$) and graphite at high temperature (above 800 °C). It was revealed by German *et al.*[28] that microhardness of Tc carbide depends on the C content and the temperature of preparation. As a matter of fact, Dridi *et al.*[44] theoretically found that the bulk moduli for TiC$_x$ and TiN$_x$ increase with the concentration of C and N, respectively, which provides extremely useful hint for understanding the discrepancy between the theoretical and experimental hardness.

The electronic structure is crucial to the understanding of the mechanical properties, and we use TcC and TcN in the WC type as an illustrative case. Shown in Fig. 3 is the calculated DOS for TcC and TcN in the WC structure. As we have seen, the substantially large total DOS at the Fermi level indicates well the metallic feature for both compounds. This metallicity might make them a better candidate for hard conductors at extreme conditions of high temperatures and high pressures. Also, we find that the electronic structures are governed by a strong hybridization between the metal 4*d* and nonmetal 2*p* states, which indicates the strong covalent bonding. The covalency can be clearly seen through the charge density for TcC of the WC phase in Fig. 4. Neighboring C atoms form very powerful covalent bonds, and the bonding between the Tc atoms and their neighboring C atoms is also highly orientational. The highly directional bonds and high valence electron densities result in high bulk modulus and hardness of TcC and TcN in the WC structure. On the other hand, we note that the DOS profiles of TcC and TcN in the WC structure in Fig. 3 are a little similar: a deep valley separates the Tc-C or Tc-N (as well as C-C or N-N) bonding and antibonding states. The states near the Fermi level for TcC in the WC structures are the nonbonding Tc 4*d* orbitals localized on the Tc atoms, while the position of the Fermi level for TcN has a right shift with the increase in valence electrons. However, the bonding states are saturated and the antibonding states to be filled increase from TcC to TcN. Because of the fact that the antibonding states soften the bonds, the elastic properties such as the bulk modulus, shear modulus, and elastic constant C_{44} decrease from TcC to TcN.

IV. CONCLUSIONS

In summary, first-principles calculations have been performed to study the structural, mechanical, and electronic

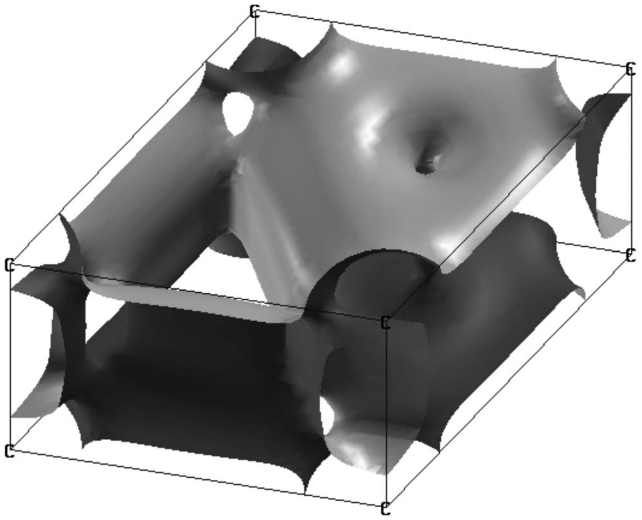

FIG. 4. Charge density for TcC in the WC structure within a primitive cell. The bondings of Tc-C and C-C exhibit the high directionality, indicating strong covalent characters.

properties of TcC and TcN in the WC, NiAs, NaCl, and ZnS structures, respectively. Our results suggest that TcC and TcN in the WC and NiAs structures are mechanically stable while the NaCl phases are mechanically unstable and that the ZnS phase of TcC displays an electronically weak stability. For the two stable hexagonal phases, both TcC and TcN are ultraincompressible and hard materials. Specially, the bulk moduli and uniaxial Young's moduli of the two hexagonal TcC compounds exceed that of *c* BN and even approach to that of diamond. Their hardness also matches the known hard materials such as WC and Al_2O_3. Such metallic and hard materials can be used in some applications such as hard conductors and cutting processes.

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