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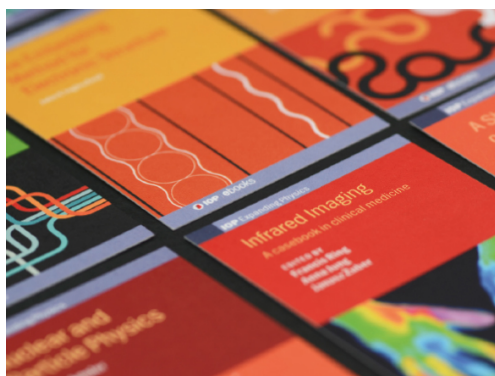
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Pressure-induced effects on elastic and mechanical properties of TiC and TiN: A DFT study

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Abstract – Pressure-induced effects on elastic, structural phase transition and mechanical properties of TiC and TiN are studied under high pressures from first-principle calculations. Calculated lattice parameters, elastic constants and theoretical Vickers hardness are in excellent agreement with available experimental and theoretical results. The transition pressure from NaCl to CsCl phase is determined with values of 5.695 Mbar for TiC and 3.482 Mbar for TiN. Pressure-induced effects on mechanical properties of NaCl-type TiC and TiN show that the Vickers hardness increases first, to a maximum value 43.65 and 27.48 GPa at the pressure of 2.1 and 0.9 Mbar for NaCl-type TiC and TiN, respectively, and then decreases with increasing pressure.

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Introduction. – Due to their excellent physical and mechanical properties: high hardness, high melting point (around 3000 °C), high electrical conductivity, face-centered cubic titanium carbide and nitride (NaCl structure) are widely applied as aerospace structural components, thin films for electronic devices and coating materials for surface protection of cutting tools [1–6]. As important precipitates for strengthening steels, it is significant to control the size distribution of titanium carbides and nitrides precipitates to obtain the desired mechanical strength of steels. This has attracted much interest of experimentalists and theoreticians. However, some of the fundamental physical properties are difficult to measure experimentally, but can be estimated relatively easily if atomic scale simulation/ calculation techniques are used. Based on density functional theory calculations, Ahuja *et al.* [7] have studied structural and elastic properties of TiC, TiN and TiO, and Yang *et al.* [8] calculated elastic properties and hardness of TiC and TiN at zero pressure and zero temperature. Zhukov *et al.* [9] have calculated energy-band structure and chemical bonding in titanium and vanadium carbides, nitrides and oxides. Price *et al.* [10] have calculated the electronic structure, equilibrium lattice constant, bulk moduli, equilibrium lattice constant and fracture properties of stoichiometric

TiC. The bonding properties of transition metal carbides and nitrides have been studied by Häglund *et al.* [11] using *ab initio* calculations.

To the best of our knowledge, the theoretical structural, elastic, electronic and mechanical properties of titanium carbide and nitride under high pressure have not been discussed systematically so far. In this work, we present a systematical study of structural, elastic, and mechanical properties of these compounds under high pressure by using the Vanderbilt ultrasoft pseudopotential method. Our main purpose is to provide more useful information on the influence of pressure on the elastic, mechanical properties and hardness of them.

Computational details. – All first-principles total energy calculations are performed using CASTEP code [12], the interactions between 3d transition metal Ti and C, N atoms are described with the Vanderbilt ultrasoft pseudo-potential [13]. The exchange and correlation functional are treated by the Perdew-Berke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) [14]. The Brillouin zone is sampled with the Monkhorst-pack scheme (15 × 15 × 15 *k*-mesh). Optimization of atomic positions and lattice parameters is achieved by minimization of forces and stress tensors. We choose a cutoff energy of 1500 eV, which gives energy convergence less than 10^{−6} eV/atom. The maximum

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Table 1: Calculated lattice constants a (Å), formation enthalpy per formula unit ΔH (eV), elastic constants C_{ij} (Mbar), bulk modulus B (Mbar), shear modulus G (Mbar), Young's modulus E (Mbar), elastic anisotropy factor A and the ratio B/G , along with experimental and other theoretical values for NaCl and CsCl structures of TiC and TiN at ambient conditions.

	NaCl-TiC			CsCl-TiC		NaCl-TiN			CsCl-TiN
	Present	Exp.	Cal.	Present	Present	Exp.	Cal.		Present
a	4.331	4.328 ^a	4.331 ^b , 4.42 ^c , 4.316 ^d	2.71	4.246	4.238 ^h , 4.242 ⁱ	4.246 ^b , 4.242 ^c		2.636
ΔH	-1.651		-1.56 ^c	0.71	-3.919		-3.48 ^c		-2.114
C_{11}	5.22	5.10 ^e , 5.00 ^f	5.19 ^b , 5.22 ^c , 6.10 ^d	0.79	5.43	6.25 ^j , 6.31 ^k	5.79 ^b , 6.59 ^c , 7.13 ^d		6.17
C_{12}	1.15	1.00 ^e , 1.13 ^f	1.15 ^b , 1.02 ^c , 1.24 ^d	2.86	1.43	1.65 ^j , 1.71 ^k	1.29 ^b , 1.50 ^c , 1.33 ^d		0.19
C_{44}	1.77	1.80 ^e , 1.75 ^f	1.83 ^b , 1.29 ^c , 1.73 ^d	-3.12	1.66	1.63 ^j , 1.70 ^k	1.80 ^b , 1.83 ^c , 1.66 ^d		0.75
B	2.51	2.42 ^f , 2.33 ^g	2.49 ^b		2.77	3.18 ^j , 2.33 ^l	2.79 ^b		
G	1.87	1.82 ^f , 1.84 ^g	1.90 ^b		1.79	1.87 ^j , 1.79 ^l	1.97 ^b		
E	4.80	4.37 ^f , 4.36 ^g	4.55 ^b		4.82	4.69 ^j , 4.27 ^l	4.77 ^b		
A	0.87	0.878 ^e , 0.91 ^f	0.91 ^b		0.83	0.71 ^a , 0.793 ^b	0.8 ^b , 0.719 ^c , 0.572 ^d		
B/G	1.342	1.33 ^f , 1.266 ^g	1.311 ^b		1.55	1.7 ^a , 1.3 ^b	1.42 ^b		

^aReference [15]; ^bref. [8]; ^cref. [1]; ^dref. [16]; ^eref. [17]; ^fref. [18]; ^gref. [19]; ^href. [20]; ⁱref. [21]; ^jref. [22]; ^kref. [23]; ^lref. [24].

force tolerance, the maximum stress, and the maximum displacement tolerance are selected as 0.01 eV/Å, 0.02 GPa, 5.0×10^{-4} Å, respectively.

Results and discussions. –

Structural, elastic properties and pressure-induced structural phase transition. TiC and TiN compounds crystallize in the rocksalt structure (NaCl-type) with the space group of $FM-3M$ (cubic system) at ambient conditions. The conventional cell contains four formula units (eight atoms). The titanium atom locates at Wyckoff site $4a$ (0, 0, 0), carbide and nitride atom at $4b$ (1/2, 1/2, 1/2). Optimized structural parameters are obtained by searching for the stable structure for a minimum total energy with suitable convergence criteria mentioned above in the “Computational details” section. Table 1 lists the calculated lattice parameter, elastic constants C_{ij} , bulk modulus B , shear modulus G , Young's modulus E , elastic anisotropy factor A and the ratio B/G for NaCl- and CsCl-type TiC and TiN at ambient conditions. It can be seen from table 1 that the present calculated lattice parameter and elastic constants for NaCl-type TiC and TiN are in good agreement with the available experimental results and previous theoretical calculations. Unfortunately, no related experimental and theoretical data are reported for CsCl-type TiC and TiN for comparison. So, our calculations can be used to cover this lack of data for this important material.

It is well known that a cubic crystal has only three independent elastic constants, namely C_{11} , C_{12} and C_{44} , which are related to the second-order change in the internal energy of a crystal under deformation. The mechanical stability criteria are given by ref. [25] as follows:

$$C_{11} - C_{12} > 0, \quad C_{11} > 0, \quad C_{44} > 0, \quad C_{11} + 2C_{12} > 0. \quad (1)$$

Obviously, the results of NaCl-TiC, TiN and CsCl-TiN in table 1 satisfy the stability criteria, indicating they are mechanically stable. In contrast, the elastic constants

of CsCl-TiC do not satisfy all the stability conditions of eq. (1), suggesting that the CsCl-TiC is mechanically unstable at ambient conditions.

Moreover, a high B/G value is associated with ductility, while a low B/G value represents brittleness [26]. The theoretical value which separates ductile and brittle materials is about 1.75. The present calculated ratios of B/G are 1.342 and 1.55 for NaCl-TiC and NaCl-TiN, respectively, and this classifies the two as brittle material.

The formation enthalpies for binary TiM ($M = C, N$) can be calculated with the following equation,

$$\Delta H = E(\text{TiM}) - E(\text{Ti}) - E(\text{M}) \quad (2)$$

where $E(\text{TiM})$ is the total energy of TiC or TiN, $E(\text{Ti})$ is the total energy of Ti bulk crystal and $E(\text{M})$ is the total energy per atom of M, for C with graphite structure and for N with gaseous structure. At zero pressure, the calculated formation enthalpy of NaCl- and CsCl-type TiC and TiN in table 1 suggests a relative stability order of NaCl-type > CsCl-type for TiC and TiN.

Since these highly hard materials are usually used at extreme conditions, it is important to study their behavior under high pressure. Here we would like to study the possibility of structural phase transitions under high pressure. It is well known that, at zero temperature, the Gibbs free energy G is equal to the enthalpy H for solids. Therefore, the estimation of the zero-temperature transition pressure can be obtained from the usual condition of equal enthalpies, in other words, the pressure P , at which the enthalpy $H = E + PV$ of both two phases is the same [27]. Our calculations show that TiC and TiN will undergo a structural phase transition from NaCl to CsCl phase with the increase of pressure. As shown in fig. 1, the intersection of two enthalpy curves implies that the phase transition occurs at 5.695 Mbar and 3.482 Mbar for TiC and TiN, respectively.

Hardness and electronic structure. Young's and shear moduli are two important quantities for technological

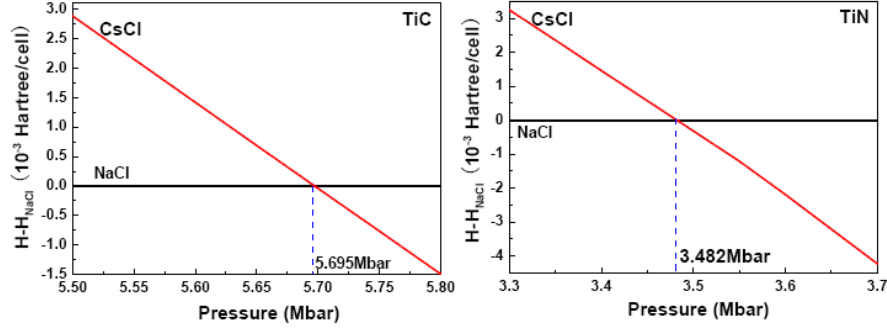


Fig. 1: (Colour on-line) Calculated enthalpy as a function of pressure for NaCl- and CsCl-type TiC, TiN at $T = 0$ K. The dashed line denotes phase transition at 5.695 Mbar for TiC and 3.482 Mbar for TiN, respectively.

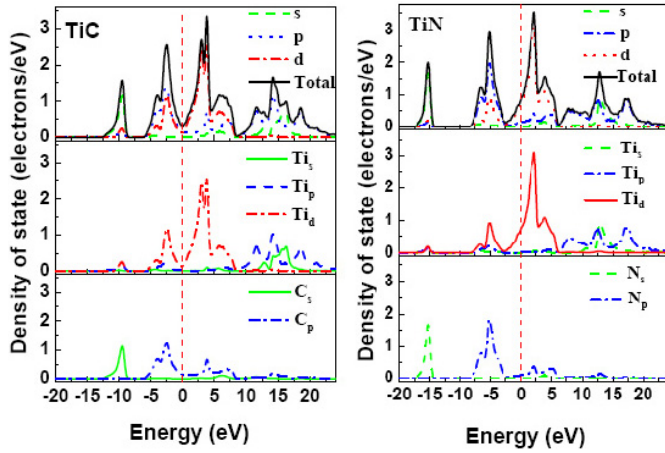


Fig. 2: (Colour on-line) Total and partial density of states (DOS) for NaCl-type TiC and TiN. The vertical dashed line at zero indicates the Fermi energy level.

and engineering applications and provide a fundamental description of a material's mechanical behavior. The shear modulus is the most important parameter governing indentation hardness. However, it is difficult to describe hardness quantitatively only by the macroscopic physical properties of Young's and shear modulus. So the prediction of hardness is of great potential interest. As shown in fig. 2, the calculated density of states (DOS) indicates that the transition-metal carbides and nitrides are metallic, and a deep valley E_P , named pseudogap, appears on the left of the Fermi level. This implies that the electrons occupying the levels above E_P become delocalized and the material is said to have metallicity. So, a correction of metallic bonding should be considered for hardness calculation of crystals with partial metallic bonding [28]. According to the work of Gou *et al.* [29], the metallicity of crystals (f_m) and the Vickers hardness (H_v) can be calculated as

$$f_m = P'/P, \quad P' = n_{free}/V, \quad n_{free} = \int_{E_P}^{E_F} N(E)dE, \quad (3)$$

$$H_v \text{ (GPa)} = A_0(P - P')v_b^{-5/3}, \quad (4)$$

Table 2: Calculated Mulliken population P , metallic population P' , metallicity f_m , the bond volume v_b (\AA^3), and Vickers hardness H_v (GPa), along with experimental values H_{exp} (GPa) for NaCl-type structure TiC and TiN.

	P	P'	f_m	v_b	H_v (GPa)	H_{exp} (GPa)
TiC	0.338	0.002	0.006	3.385	32.58	32 ^a , 26–34 ^b
TiN	0.280	0.054	0.193	3.190	24.19	23 ^c , 19.7 ^d

^aReference [18]; ^bref. [30]; ^cref. [31]; ^dref. [32].

where P is the Mulliken population, P' is the metallic population, n_{free} is the number of effective free electrons in a cell, V is the volume of the cell, $N(E)$ is the DOS, E_F is the Fermi energy. A_0 , a proportional coefficient, is set to 740, and v_b is the bond volume. At zero pressure, the related results of the NaCl-type structures TiC and TiN are listed in table 2, and one can see that the calculated Vickers hardness results are in good agreement with the experimental values, which indicate that TiC possesses higher hardness than TiN compounds in the NaCl-type structure. There is the possibility that TiC has a weaker metallic property in comparison with TiN, due to its few electronic bands crossing the Fermi level, which has a very low electronic density of states around Fermi level as seen from fig. 2.

Pressure-dependent elastic and mechanical properties.

As for the pressure dependence behaviors of TiC and TiN compounds, we concentrate on pressures ranging from zero to the theoretical calculated transition point ($0 \rightarrow P_t$). Figure 3 plots the dependence of elastic constants, bulk modulus B , shear modulus G , and Young's modulus E on hydrostatic pressure. It is found that all of the elastic constants and moduli increase monotonically with pressure, and the values of C_{11} , C_{12} , bulk modulus B , and Young's modulus E vary substantially under pressure. In contrast, those of C_{44} and shear modulus G increase slowly. The elastic anisotropy at high pressure is important for understanding the evolution of bonding in a system. A measure of the anisotropy of elasticity is $A = 2C_{44}/(C_{11} - C_{12})$ for cubic crystals. For

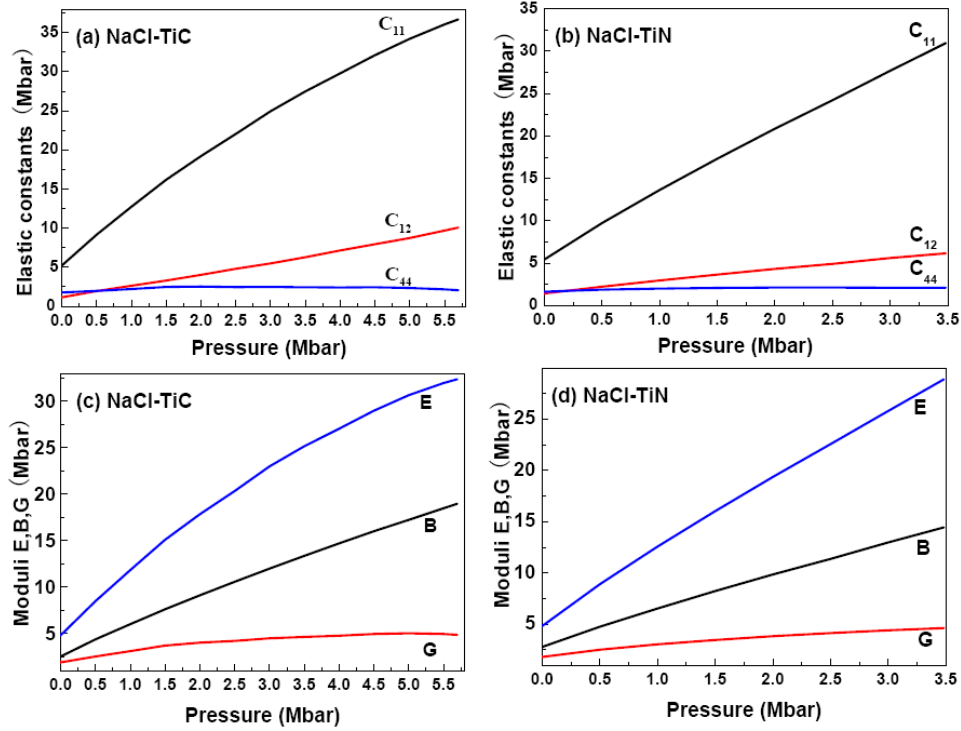


Fig. 3: (Colour on-line) Pressure dependence of elastic constants, bulk modulus B , shear modulus G , and Young's modulus E for NaCl-type TiC and TiN considering the pressure from zero to the phase transition pressure ($0 \rightarrow P_t$).

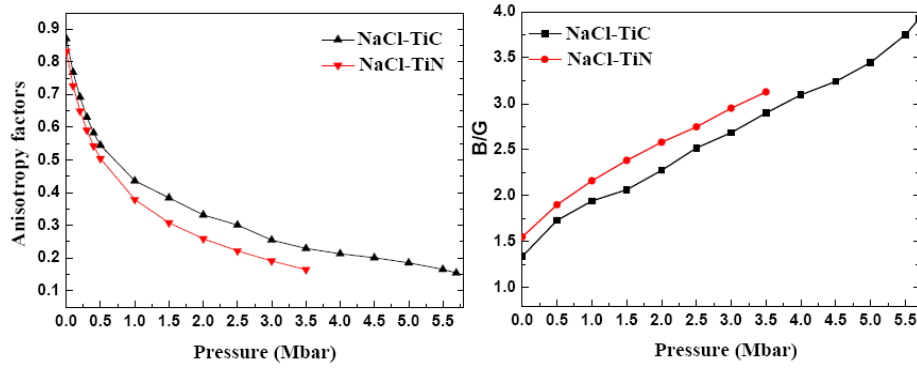


Fig. 4: (Colour on-line) Pressure dependence of the anisotropic factor and the ratio B/G for NaCl-type TiC and TiN considering the pressure from $0 \rightarrow P_t$.

isotropic elasticity, the two shear moduli $(C_{11} - C_{12})/2$ and C_{44} are equal and the anisotropy becomes unity. In fig. 4, we have plotted the variation of the anisotropic factor and the ratio B/G of NaCl-type TiC and TiN crystals at different pressures. One can see from fig. 4 that NaCl-type TiC and TiN crystals are elastically anisotropic and this behavior decreases with the increase of the pressure. Moreover, it is shown that the B/G values increase monotonically with pressure. This indicates that NaCl-type TiC and TiN maybe change from brittle to ductile with pressure increasing.

Figure 5 presents the dependence of the calculated Vickers hardness on hydrostatic pressure and it is clear that the calculated Vickers hardness increases first with increasing pressure, and reaches a maximum value of 43.65 and 27.48 GPa at the pressure of 2.1 and 0.9 Mbar for NaCl-type TiC and TiN, respectively, then it decreases. It is reported in the work of Antonín Šimůnek that the hardness of the ideal single crystal is proportional to the bond strength and the bond number in the unit cell of the crystal, where the bond strength is inversely proportional to the bond distance [33]. To clearly understand

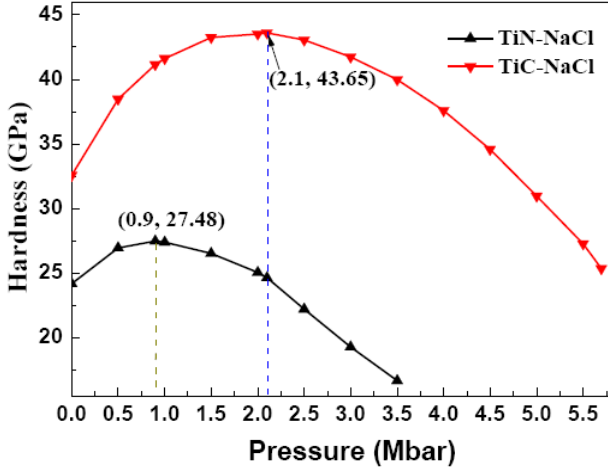


Fig. 5: (Colour on-line) Pressure dependence of the Vickers hardness for NaCl-type TiC and TiN considering the pressure from $0 \rightarrow P_t$.

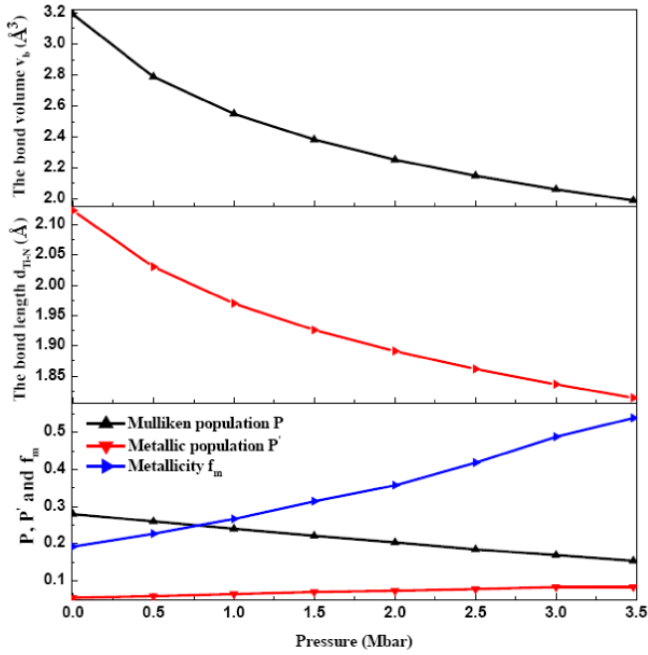


Fig. 6: (Colour on-line) Calculated bond volume v_b , bond length d_{Ti-N} , Mulliken population P , metallic population P' and metallicity f_m for NaCl-type TiN under high pressure.

the effect of high pressure on hardness, we plot the calculated bond volume v_b , the bond length d_{Ti-N} , the Mulliken population P , the metallic population P' and metallicity f_m as a function of the pressure for TiN (see fig. 6). From fig. 6, one can see that the bond length decreases substantially with pressure increasing to 0.9 Mbar, as a result of the bond strength becoming stronger. This suggests that the hardness increases with the pressure in the range of 0–0.9 Mbar. For pressures higher than 0.9 Mbar, the bond length decreases slightly with the pressure, while the metallic component of the bond (f_m) increases

significantly with increasing pressure as shown in fig. 6. This implies that the hardness decreases with higher pressures because the metallic component of the bond (f_m) has a stronger negative effect on hardness. In the above, the hardness increases with pressure up to 0.9 Mbar, and then decreases with increasing pressure to 3.5 Mbar for TiN. Unfortunately, there are no experimental data available related to these materials for comparison so far. We hope that in the near future there will be more high-pressure measurements on these technologically important materials.

Conclusions. – Using DFT calculations, we have studied the elastic, mechanical properties under high-pressure and pressure-induced structural transition of titanium carbides and nitrides. The main results are summarized as follows:

- i) The structural parameters, elastic and mechanical properties for both TiC and TiN are in good agreement with available experimental and theoretical results. Pressure-dependent properties indicate that as the pressure increases, NaCl-type TiC and TiN may change from brittle to ductile material.
- ii) Present calculations predict a NaCl \rightarrow CsCl structural phase transition at pressures of 5.695 and 3.482 Mbar for TiC and TiN, respectively. Careful experimental investigations are needed to clarify the NaCl \rightarrow CsCl structural phase transition.
- iii) Pressure-dependent hardness results of NaCl-type structure TiC and TiN show that as the pressure increases, theoretical Vickers hardness increases first to a maximum value, and then decreases. In contrast, the bulk modulus or the shear modulus increase monotonically with increasing pressure. This suggests that there is no one-to-one correspondence between hardness and bulk modulus or shear modulus.

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