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First-Principles Investigations on Structure Transformation, Elastic and Thermodynamic Properties of TiN under High Pressure*

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Abstract: An investigation on the structure transformation, elastic and thermodynamic properties of TiN under high pressure is conducted using first-principles calculations based on density functional theory (DFT) with the plane wave basis set. At elevated pressures TiN is predicted to undergo a structural phase transition from a relatively open NaCl-type (B1) structure into a denser CsCl-type (B2) structure. The predicted transition pressure is 348 GPa. The elastic constants, Debye temperature, and heat capacity each as a function of pressure and/or temperature of TiN are presented.

Key words: elastic property; thermodynamic property; high pressure; *ab initio* calculations

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1 Introduction

The transition metal nitrides have attracted considerable attention during the past four decades due to their interesting combination of mechanical, electrical, and chemical properties. These lead to their wider and wider application as hard coatings and thin films for electronic devices. In particular, their high activation energy against electromigration, coupled with superior electrical conductivity, high melting point, and excellent chemical stability has made these "refractory hard metals" extensively used for semiconductor and photovoltaic technology, and desirable candidates for new materials in electronic devices[1-5].

Harrison *et al*.[6] studied the electronic structure and properties of *d*- and *f*-shell-metal compounds with the rocksalt structure. Their results show that the simplest systems with 8 valence electrons per atom pair are almost insulating; and for the system with 9-12 valence electrons, the excess electrons occupy nonbonding bands making the compound metallic. Ahuja *et al*.[7] studied the struc-

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tural and elastic properties of TiC, TiN, and TiO by means of accurate first-principles total-energy calculations using the full potential linear muffin-tin orbital method.

First-principles calculations using the full-potential linearized augmented plane wave method are performed to investigate the bulk electronic and physical properties of a series of early transition metal mononitrides in the rocksalt structure[8]. Lazar *et al*.[9] reported the materials properties of VN/TiN mutilayers focusing on the elastic and mechanical properties of the interface. Modeling of the mechanical properties was done in terms of brittle cleavage by calculating cleavage energies and critical stresses for the bulk phases as well as the multilayer system. Che *et al*.[10] studied the equation of state, electronic and phonon band structure of TiN under high pressure using the pseudopotential plane-wave method and linear response theory within the density functional theory.

As stated above, different theoretical calculations of TiN bulk electronic, elastic properties have been compared and discussed extensively. To date, there are only a few reports in literatures about the pressure-induced structural transition of TiN and no study on the thermodynamic properties of TiN. Therefore, there is a need to investigate the elastic and thermodynamic properties of TiN under simulated extreme working conditions.

2 Computational Details and Theory

2.1 Computational Details

Our first-principles calculations are performed with the CASTEP code in MS modeling based on the plane wave basis set[11], the ultrasoft pseudopotential for electron-ion interaction, and the exchange correlation potential of Perdew *et al*.[12] in the generalized gradient approximation (GGA) for electron-electron interaction. The typical configurations are $3s^2 3p^6 3d^2 4s^2$ and $2s^2 3p^3$ for Ti and N, respectively. Integrations in the Brillouin zone are performed using special k points generated with $14\times14\times14$ for NaCl-type (B1) and CsCl-type (B2) structures, which make the separation of reciprocal space be less than $0.2\ \mathrm{nm}^{-1}$. One-electron valence states are expanded on a basis of plane waves with a cutoff energy of 700 eV in the electronic property calculations. Such parameters have been tested to be sufficient for convergence ($<10^{-3}$ eV). During the structure optimization, the total energy is minimized by varying cell parameters and atomic positions under the restriction of the given symmetry. In the geometrical optimization, all forces on atoms are converged to less than 0.01 eV/nm, and the total stress tensor is reduced to the order of 0.005 GPa by using the finite basis-set corrections[13].

2.2 Elastic Properties

The elastic constants are defined by means of a Taylor expansion of the total energy $E(V,\delta)$ for the system with respect to a small strain δ of the lattice primitive cell volume V. The energy of a strained system is expressed as[14]

$$E(V,\delta) = E(V_0,\delta) + V_0\left(\sum_i \tau_i \xi_i \delta_i + \frac{1}{2}\sum_{ij} C_{ij}\delta_i\xi_i\delta_j\xi_j\right) \tag{1}$$

where $E(V_0,\delta)$ is the energy of the unstrained system with equilibrium volume V_0, τ_i is an element in the stress tensor, ξ_i and ξ_j are factors of Voigt index.

2.3 Thermodynamic Properties

In order to obtain the thermodynamic properties of VN, the quasi-harmonic Debye model[15] is introduced, in which the non-equilibrium Gibbs function $G^*(V,p,T)$ takes as

$$G^*(V,p,T) = E(V) + pV + A_{\mathrm{vib}}[\Theta_{\mathrm{D}}(V),T] \tag{2}$$

here $E(V)$ is the total energy per unit cell, $\Theta_{\mathrm{D}}(V)$ is the Debye temperature, p is pressure, T is tem-

perature, and the vibrational Helmholtz free energy $A_{\mathrm{vib}}(\Theta_{\mathrm{D}}, T)$ can be written as[16]

$$A_{\mathrm{vib}}(\Theta_{\mathrm{D}}, T) = nKT\left[\frac{9}{8}\frac{\Theta_{\mathrm{D}}}{T} + 3\ln(1-\mathrm{e}^{-\Theta_{\mathrm{D}}/T}) - D\left(\frac{\Theta_{\mathrm{D}}}{T}\right)\right] \tag{3}$$

where $D(\Theta_{\mathrm{D}}/T)$ represents Debye integral, n is the number of atoms per formula unit, k is Boltzmann constant. For an isotropic solid, Θ_{D} is expressed as

$$\Theta_{\mathrm{D}} = \frac{\hbar}{k}(6\pi^2 V^{1/2} n)^{1/3} f(\sigma)\left(\frac{B_S}{M}\right)^{1/2} \tag{4}$$

here M is the molecular mass per formula unit, B_S is the adiabatic bulk modulus, which can be approximated by the static compressibility, namely

$$B_S \approx B(V) = V\left(\frac{\mathrm{d}^2 E(V)}{\mathrm{d}V^2}\right) \tag{5}$$

and $f(\sigma)$ is given as[17]

$$f(\sigma) = \left\{3\left[2\left(\frac{2}{3}\frac{1+\sigma}{1-\sigma}\right)^{3/2} + \left(\frac{1}{3}\frac{1+\sigma}{1-\sigma}\right)^{3/2}\right]^{-1}\right\}^{1/3} \tag{6}$$

where σ is Poisson ratio. Therefore, the non-equilibrium Gibbs function $G^*(V, p, T)$ as a function of (V, p, T) can be minimized with respect to volume V as

$$\left(\frac{\partial G^*(V, p, T)}{\partial V}\right)_{p,T} = 0 \tag{7}$$

By solving Eq. (7), we can obtain the thermal equation of state $V(p, T)$. The isothermal bulk modulus is given as

$$B_T(p, T) = V\left[\frac{\partial^2 G^*(V, p, T)}{\partial V^2}\right]_{p,T} \tag{8}$$

The heat capacity at constant volume C_V is taken as

$$C_V = 3nk\left[4D(\Theta_{\mathrm{D}}/T) - \frac{3\Theta_{\mathrm{D}}/T}{\mathrm{e}^{\Theta_{\mathrm{D}}/T} - 1}\right] \tag{9}$$

3 Results and Discussion

3.1 Structural Properties

The total energy as a function of volume is calculated to determine the equilibrium volume and bulk modulus by parabolic fitting to a third-order Birch-Murnaghan equation of state[18]. The calculated equilibrium lattice constant and bulk modulus of TiN in B1 and B2 structures are illustrated in Table 1. It can be clearly seen that the calculated structural parameters are in agreement with experimental results[19] and other theoretical investigations[10,20-21]. For bulk modulus of TiN-B1, the results are consistent with previous theoretical results[10,20-21].

Table 1 Calculated equilibrium lattice constant (a_0), energy gap (E_g) and bulk modulus (B) of TiN, together with previous results

Structure	a_0/(nm)	E_g/(eV)	B/(GPa)	B'
TiN-B1	0.424 6, 0.425[10], 0.426 0[19], 0.424 0[20], 0.425 3[21]	0	277, 263[10], 320[19], 305[20], 280[21]	4.12, 4.1[10]
TiN-B2	0.263 6	0	244	4.13

Our computational approach is based on constant-pressure static quantum mechanical calculations at $T=0$ K, so the relative stability of different structures can be deduced from the pressure dependence of the enthalpy instead of the Gibbs free energy[22]. The calculation suggests that there exists a transition from B1 to B2 structure, which is a second-order phase transition. The pressure corresponding to

$\Delta H = H_{B2} - H_{B1}$ approaching zero is the transition pressure, as shown in Fig. 1. The calculated transition pressure and volume collapse are 348 GPa and 6.5%, respectively.

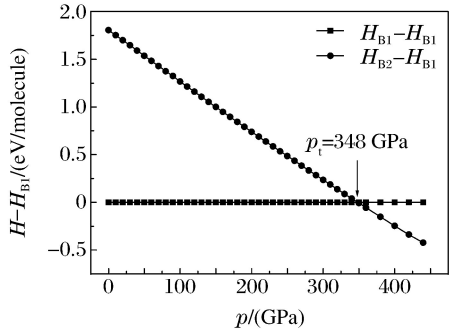


Fig. 1 Calculated enthalpies for the B2 phase of TiN relative to that of the B1 phase as a function of pressure

3.2 Elastic Properties

The elastic constants of solids provide a link between the mechanical and dynamics, and provide important information concerning the nature of the forces operating in solids. In particular, they offer information on the stability and stiffness of materials. The total energy of the system depends on volume more strongly than on strain. In this work, the volume contribution to total energy can be eliminated using volume conserving strains. The systems are fully relaxed after each distortion in order to reach the equilibrium state with approximately zero forces on all atoms[23].

The elastic constants of TiN in B1 and B2 structures at ambient pressure are tabulated in Table 2. For B1 structure, our results are in reasonable agreement with experimental results[24] and other theoretical investigations[1]. The traditional mechanical stability conditions of the elastic constants in cubic crystal are $C_{11}-C_{12}>0$, $C_{11}>0$, $C_{44}>0$, $C_{11}+2C_{12}>0$, $C_{12}<B<C_{11}$. For TiN-B1, the elastic constants satisfy these stability conditions, indicating that the B1 structure is a mechanically stable phase at ambient pressure. For TiN-B2 structure, since there is no other report on the elastic constants up to now, we could not compare our results with other results.

Table 2 The elastic constants and Poisson ratio σ of TiN at ambient pressure

Structure	C_{11}	C_{12}	C_{44}	σ
TiN-B1	585, 585[1], 625[24]	123, 137[1], 165[24]	152, 165[1], 63[24]	0.23
TiN-B2	636	64	14	0.37

We further investigate the high-pressure elastic behavior of TiN-B1, by computing the second-order elastic constants (SOECs) and their variations with pressure, as shown in Fig. 2. It is noticed that C_{11} and C_{12} increase linearly with pressure. C_{11} is more sensitive to the change of pressure compared to C_{12}. The bulk modulus B increases gradually with pressure, indicating it becomes more and more difficult to be compressed with increasing pressure.

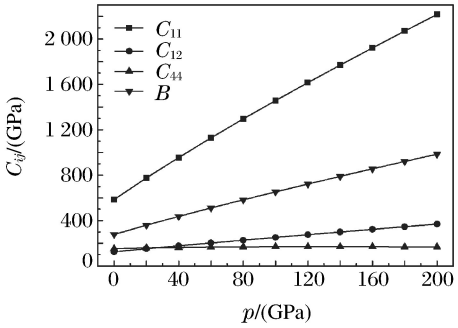


Fig. 2 The elastic constants as a function of pressure of TiN-B1

A simple relationship, which empirically connects the plastic properties of materials with their elastic moduli, was proposed by Pugh[25]. The shear modulus G represents the resistance to plastic deformation, while B represents the resistance to fracture[26]. A high B/G ratio is associated with ductility, whereas a low value corresponds to the brittle nature. The critical value which separates ductile and brittle material is 1.75; i.e., if $B/G>1.75$, the material behaves in a ductile; otherwise the materi-

al behaves in a brittle manner. Our results show that B/G is 1.54 for TiN-B1 at ambient conditions, classifying it into being brittle.

The elastic anisotropy of crystal has an important implication in engineering science since it is highly correlated with the possibility to induce microcracks in materials[27]. The anisotropy factor $A=(2C_{44}+C_{12})/C_{11}$ has been evaluated to provide insight on the elastic anisotropy. For an isotropic crystal A equals 1, while any value smaller or larger than 1 indicates anisotropy. The magnitude of a deviation from 1 is a measure of the degree of elastic anisotropy possessed by the crystal. For TiN-B1, A equals 0.73, indicating that it cannot be regarded as elastically isotropic due to the A values smaller than 1.0.

3.3 Thermodynamic Properties

The pressure and temperature dependence of the isothermal bulk modulus for TiN-B1 is shown in Fig. 3. It demonstrates that the dramatic volume variation leads to the rapid decrease in the isothermal bulk modulus. These results indicate that B increases with p at a given temperature and decreases with T at a given pressure. It shows the fact that the effect of increasing pressure on TiN is the same as that of decreasing temperature. However, the effect of temperature on the bulk modulus is less important than that of pressure.

The pressure and temperature dependence of Debye temperature for TiN-B1 is shown in Fig. 4. It demonstrates that the dramatic volume variation leads to the rapid decrease in Debye temperature. These results indicate that the Debye temperature increases with p at a given temperature and decreases with T at a given pressure.

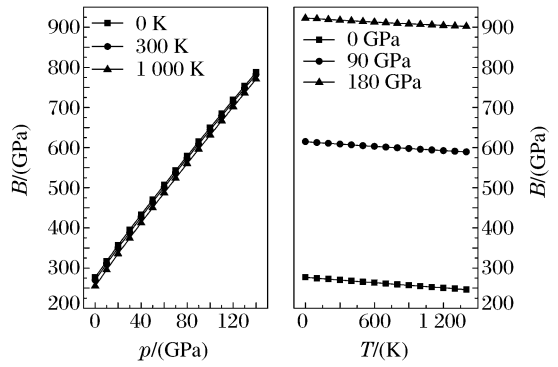


Fig. 3　Pressure and temperature dependence of bulk modulus of TiN-B1

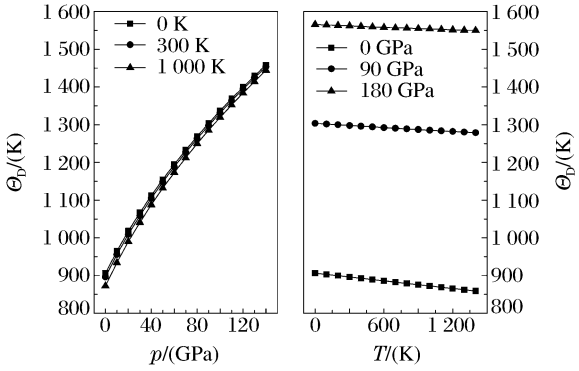


Fig. 4　Pressure and temperature dependence of Debye temperature of TiN-B1

The other thermodynamic parameter, heat capacity, is also very important. Through heat capacity C_V, we can obtain the information about lattice vibrations, energy band structure, density of state, transition of phase of the solid, etc. In Fig. 5, the variation curves of the heat capacity of TiN-B1 with temperature and pressure are presented. At sufficiently low temperatures ($T<50$ K), C_V is proportional to T^3. The density of states of the acoustic phonons at low phonon frequencies influences the low-temperature behavior of the lattice

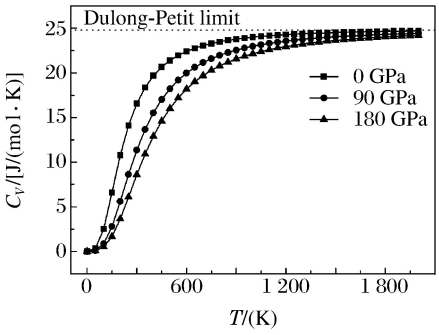


Fig. 5　The heat capacity of TiN-B1 at various pressures and temperatures

specific heat. Debye's T^3 law, which is due to the long-wavelength acoustic phonons, should be valid in this temperature region. At higher temperatures this contribution to the lattice specific heat increases exponentially with temperature in a manner similar to the Einstein model. These curves show that C_V has a quantum behavior at low temperatures and a classical behavior at high temperatures.

4 Conclusions

The structure transformation, elastic and thermodynamic properties of TiN are studied using first-principles calculations. The calculated structural and elastic parameters agree well with the available experimental results and the previous theoretical data. It is predicted that the B1 to B2 transition pressure of TiN is 348 GPa. The fundamental physical properties, such as elastic constants, Debye temperature, and heat capacity as a function of pressure and/or temperature of TiN are also presented and discussed.

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高压下 TiN 的结构转变、弹性和热力学性质的第一性原理计算

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摘要: 利用基于密度泛函的第一性原理, 计算了高压下 TiN 的结构转变、弹性和热力学性质。计算结果表明: 在压力作用下, TiN 经历了从 NaCl 型结构到 CsCl 型结构的转变, 转变压力为 348 GPa; TiN 的弹性系数随着压力的增加呈线性增加规律。此外, 还给出了德拜温度和热容量这两个重要热力学量与温度和(或)压力的依赖关系。

关键词: 弹性; 热力学性质; 高压; 第一性原理计算

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