



Phase stability, electronic structure and equation of state of cubic TcN from first-principles calculations



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ABSTRACT

The phase transition, electronic band structure, and equation of state (EOS) of cubic TcN are investigated by first-principles pseudopotential method based on density-functional theory. The calculated enthalpies show that TcN has a transformation between zincblende and rocksalt phases and the pressure determined by the relative enthalpy is 32 GPa. The calculated band structure indicates the metallic feature and it might make cubic TcN a better candidate for hard materials. Particular attention is paid to the predictions of volume, bulk modulus and its pressure derivative which play a central role in the formulation of approximate EOSs using the quasi-harmonic Debye model.

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1. Introduction

In the quest for superhard materials widely used in cutting and coating industries, attention has been drawn to transition-metal nitrides. Hard coatings of many transition metal nitrides have ubiquitous applications in manufacturing and semiconductor industries because of their extreme hardness, wear and corrosion resistance, and suitable thermal and electrical properties [1–3]. Among these compounds, some promising candidates have been experimentally synthesized and studied. Especially lately, four noble-metal nitrides – osmium nitride (OsN₂) [4,5], iridium nitride (IrN₂) [5,6], platinum nitride (PtN₂) [6,7], and palladium nitride (PdN₂) [8] have been synthesized successfully under high pressure and high temperature. Apart from PdN₂, all these high pressure forms can be recovered at ambient conditions. Recent first-principles investigations predicted OsN₂ and IrN₂ to be hard [9,10] which with the high bulk modulus of 358 GPa and 428 GPa respectively in experiment.

In order to hunt for new hard materials, researchers start to look closely at other transition-metal elements surrounding Os,

such as technetium (Tc) in the periodic table. The basic properties of the radioelement Tc, discovered by Perrier and Segre in 1937 [11], were known by the mid-1970s, from the early studies of its crystallographic structure, mechanical properties, superconducting properties, electrical resistivity, magnetic susceptibility, thermal diffusivity, and thermodynamic properties [12–17]. As many properties and phenomena are ultimately controlled by the crystal structures, the prediction of crystal structure is an important task in chemistry and condensed matter physics. One way to predict structure is by extracting known structures from databases of structures previously found in similar materials [18]. As we know now, many transition-metal nitrides and carbides exist in zincblende (ZB) and rocksalt (RS) structures. Experiments of Gregoryanz et al. [7] reported that PtN, the first noble transition-metal nitride to be synthesized, was also a ZB structure. Then another potential superhard material PtC was successfully synthesized under high-pressure and high-temperature and characterized by Ono et al. [19] and they concluded that PtC has also a cubic RS type structure by analyzing the synchrotron X-ray diffraction pattern. In fact, due to the large mass difference between 4d and 5d transition-metal and nitrogen elements, the only X-ray diffraction analysis is not sufficient to distinguish ZB and RS structures from each other. Some very recent works clarify this issue from different aspects: the total energy as a function of volume, the Gibbs free energy as a function of pressure, and the electronic

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band structures, and their accurate first-principle calculations indicate that PtC is crystallized in the ZB structure at zero pressure and that the RS structure is a high-pressure phase [20–22]. For Tc–N system, Tc nitrides were synthesized by hydrogen reduction of HN_4TcO_4 in ammonia at 900–1100 °C or by thermal decomposition of $(\text{NH}_4)_2[\text{TcCl}_6]$ or $(\text{NH}_4)_2[\text{TcBr}_6]$ at 380 °C under argon atmosphere in 1964 [23], and the Tc–N phases were found to crystallize in the face-centered-cubic structure (FCC) with a lattice constant varying from 3.980 to 3.985 Å according to nitrogen content. In theory research, Weck et al. [24] and Rajeswarapalanichamy et al. [25] found that ZB structure was the energetically most stable phase.

In view of the scarce information available on TcN, we provide here from first-principles calculations in the framework of density functional theory (DFT) for geometry optimization and energy–volume equation of state (EOS) on one hand and a detailed inspection of the electronic band structures on the other hand for the selected ZB and RS structures. The results show that TcN has a transformation between ZB and RS phases with the pressure increasing. On the basis of the phase transition, the dependences of the Debye temperature, Grüneisen parameter, volume, isothermal bulk modulus and its pressure derivative which play a central role in the formulation of approximate EOSs on pressure and temperature for cubic TcN are successfully predicted through the quasi-harmonic Debye approximation model [26] in which the phononic effects are considered.

2. Computational methodology

In the present work, first-principles and quasi-harmonic Debye model methods are employed to estimate electronic and thermodynamic properties under high pressure and temperature. The calculations of all total energy and geometry optimization are performed by the CASTEP code [27] which is based on DFT. The exchange–correlation effects are taken into account within the Ceperley–Alder scheme [28] in the local density approximation (LDA) [29]. To describe interactions between electrons and core ions, the Vanderbilt ultrasoft pseudopotentials are used [30]. Pseudo-atomic calculations are performed for Tc: $4s^2 4p^6 4d^6 5s^1$ and N: $2s^2 2p^3$. The electronic wave function is expanded in a plane-wave basis set with a well converged cutoff energy of 500 eV for all cases. The Brillouin zone integrations are performed using $14 \times 14 \times 14$ k -points mesh sampling. The chosen plane-wave cutoff and the number of k -points are checked carefully for convergence to obtain the correct results.

The GIBBS quasi-harmonic Debye approximation [26] has been implemented to calculate the EOS parameters including Debye temperature θ_D , Grüneisen parameter γ , volume V , isothermal bulk modulus K and its pressure derivative K' for cubic TcN. This approach does not require large supercell calculations at reduced computational cost since it relies merely on first-principles calculations of the energy as a function of unit cell volume. It is thus much more tractable computationally and is eminently suited to investigating the thermodynamic properties of entire classes of materials in a highly automated fashion, in order to identify promising candidates for more in-depth experimental and computational analysis. The details of this model and its applications have been described elsewhere [31–33]. Here we summarize the method briefly.

In thermodynamics, the equilibrium state of a system at a constant pressure and temperature minimizes its Gibbs free energy

$$G(\vec{x}; p, T) = E(\vec{x}) + pV(x) + A_{vib}(\vec{x}; T), \quad (1)$$

where \vec{x} is a configuration vector containing all the information about the system's geometry, E is the total energy of the crystal

and A_{vib} is the vibrational Helmholtz free energy. In the quasi-harmonic approximation, the Helmholtz vibrational energy can be written in the form

$$A_{vib}(\vec{x}; T) = \int_0^\infty \left[\frac{\hbar\omega}{2} + k_B T \ln\left(1 - e^{-\frac{\hbar\omega}{k_B T}}\right) \right] \times g(\vec{x}; \omega) d\omega, \quad (2)$$

where $g(\vec{x}; \omega)$ is the phonon density of states and k_B , \hbar , and ω are the Boltzmann constant, the Planck constant, and the vibrational frequency respectively. Calculation of the full phonon density of states is computationally demanding and here uses a quasi-harmonic Debye model [26] where the Helmholtz free energy is expressed in terms of the Debye temperature θ_D

$$A_{vib}(\theta_D; T) = nk_B T \left[\frac{9}{8} \frac{\theta_D}{T} + 3 \ln\left(1 - e^{-\frac{\theta_D}{T}}\right) - D\left(\frac{\theta_D}{T}\right) \right], \quad (3)$$

where $D\left(\frac{\theta_D}{T}\right)$ represents the Debye integral, n is the number of atoms per formula unit. For an isotropic solid, changes in the geometry can be treated as isotropic changes in the volume, such that the magnitude of the configurational vector \vec{x} is equal to the cube root of the volume. The value of θ_D can thus be calculated as

$$\theta_D = \frac{\hbar}{k_B} \left[6\pi^2 V^{\frac{1}{3}} n \right]^{\frac{1}{3}} f(\sigma) \sqrt{\frac{K_S}{M}}, \quad (4)$$

where σ is the Poisson ratio and it has been assumed that it is a constant, M is the mass of the unit cell, K_S is the adiabatic bulk modulus which measures the compressibility of the crystal for fixed quantum state populations and can be approximated by the static compressibility

$$K_S \approx K_V = V \left(\frac{\partial^2 E(V)}{\partial V^2} \right). \quad (5)$$

The Gibbs free energy of the system can be expressed as a function of the unit cell volume

$$G^*(V; p, T) = E(V) + PV + A_{vib}(\theta_D(V); T), \quad (6)$$

where θ_D as a function of volume is evaluated from Eqs. (4) and (5), and $E(V)$ is the total energy per unit cell for TcN and obtained from the DFT calculations for selected unit cells with different volumes. Minimizing the Gibbs free energy with respect to volume as follows

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

then the equilibrium configuration at (p, T) is determined, and additional properties, including the isothermal bulk modulus K etc. can be evaluated easily.

3. Results and discussion

To check the stability of the structures predicted from a thermodynamic perspective, the Gibbs free energy $H = E_0 + PV + TS$ must be calculated at finite temperature. In the present work, all geometry optimization and total energy calculations of the selected structures for TcN with ZB and RS phases are performed at zero temperature. Therefore, the Gibbs free energy becomes the enthalpy, $H = E_0 + PV$, where E_0 is the internal energy of the system. We calculate the enthalpy of the two-ion primitive cell of TcN in both cubic structures as a function of pressure from 0 to 80 GPa, as shown in Fig. 1. In the inset, the relative enthalpy versus pressure is presented. From Fig. 1, we can see that the ZB structure is the most energetically favorable phase at low pressure, whereas the RS structure is a high-pressure phase and the

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