

Structural phase transition and electronic properties of TiN and NbN : *ab-initio* calculation

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Abstract The structural phase transition and electronic properties of two Transition metal Nitrides (TMN: TM = Ti and Nb) from the NaCl structure to the CsCl structure are investigated theoretically using the self-consistent tight binding linear muffin orbital method. It is found that these compounds show metallic behavior under ambient condition and undergo a structural phase transition from the NaCl structure to the CsCl structure in the pressure range 290-392 GPa. The calculated ground state properties such as lattice parameter and bulk modulus are in good agreement with the available theoretical and experimental results.

Key Words Transition metal compounds, electronic band structure; electronic properties, phase transition

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1 Introduction

The transition metal nitrides are refractory compounds and put forward a technologically important series of materials. The transition metal compounds (TMC), which crystallize in NaCl (B_1) structure at ambient pressure, have been a topic of great interest because of their interesting properties. The compounds of transition metals have unusual combinations of physical properties [1]. They have high melting point and extreme hardness, which are typical of covalent crystals. For instance, the melting temperature (about 4200°C) of TaC is the highest among known materials [2]. The type of the bonding found in TMC systems is not typically ionic but more covalent [3] and the occurrence of ionic-like structure in combination with covalent-like hardness is very interesting. Due to great deal of attentions on transition metal nitrides (TMN), several research groups have studied the physical properties of TMN theoretically and experimentally. Chen et al. [4] conducted the experiments on the high-pressure phonon spectra of transition-metal nitrides HfN, ZrN and NbN by Raman-scattering. Later using Raman scattering and

X-ray diffraction Chen et al. [5] reported a quantitative study of pressure effects on the super conducting transition temperature T_C which increase initially with pressure and then saturates up to 42 GPa. The equation of states, elastic properties and hardness of TMN (TM = Zr, Nb and Hf) [6] are investigated by angle-dispersive synchrotron powder X-ray diffractometry with a diamond anvil cell. It is found that NbN crystallized cubic structure and also have hexagonal structure experimentally [7]. The electronic structure of hex-NbN and NaCl-NbN are measured by X-ray photoemission spectroscopy and ellipsometric measurements [8]. Theoretically, the phase transition (NaCl \rightarrow CsCl) and elastic properties of the selected transition metal nitrides are studied by two body Interionic potential theory [9]. The thermo physical properties of transition metal carbides and nitrides with NaCl structure were calculated using the Debye-Gruneisen model combined with *ab initio* calculation [10]. The elastic constants and electronic structure of transition metal nitrides and carbides are calculated using *ab initio* density functional perturbation theory [11]. The electronic structure and bonding mechanism of NbN and NbC are studied by means of the accurate first-principles total energy calculations using the full potential linearized augmented plane wave method (FP-LMTO) [12]. Zhao et al. [13] investigated the behavior of TiN using axial X-ray diffraction under high pressure to 30.1 GPa. Their experimental results suggest that isostructural phase transition at about 7 GPa occurs due to the discontinuity of V/V_0 data with pressure. Ahuja et al. [14], with the LDA approximation, studied the structural phase transition of TiN from NaCl-structure to CsCl-structure at 370 GPa. Chuhan et al. [15] by using the three body potential model (TBPM) approach, predicted that the phase transition pressure occurs at 310 GPa and found that the magnitude of relative volume change at the transition pressure lies at 9%. Liu et al. [16], with the first principle plane wave pseudopotential density functional theory method (DFT), predicted the phase transition of TiN at 364.1 GPa. Li et al. [17], with the *ab initio* total-energy calculations within the framework of density functional theory (DFT), predicted the phase transition of NbN at 290 GPa. So far, there has been considerable controversy for the phase transition of TiN and NbN.

In this paper, the ground state electronic and structural properties for B_1 -type TMN (TMN: TM = Ti and Nb) compounds are studied by the first principles tight binding linear muffin tin orbital (TB-LMTO) method. We show that these solids crystallize in NaCl-type structure. At high pressure, they undergo a first-order structural phase transition from the B_1 to B_2 phase in the pressure ranges 301.7 and 291 GPa respectively. We further report the electronic band structure (BS) and density of states (DOS). The organization of this paper is as follows: Section 2 describes the method of calculation of electronic BS and phase- transition pressure. In section 3, potentially interesting results with some predictions are discussed. The corresponding Sections 3.1 and 3.2 deal with the structural and electronic properties of TMN at ambient and at high pressure, respectively. Finally in Section 4, we have recapitulated the results.

2 Method of Calculation

The total energy, BS and DOS for two TM nitrides TMN (TM = Ti and N) are calculated using a similar procedure as reported in our pervious work [18-20] using the TB-LMTO method [21, 22] within the local density approximation (LDA) [23]. Van Barth and Hedin [24] parameterization scheme has been

used for exchange correlation potential. These TMN compounds crystallize in the NaCl-type structure (fcc lattice with space group, Fm3m, No. 225). In the NaCl structure, the TM and Nitrogen atoms are located at the position: TM: (0, 0, 0) and N: (0.5, 0.5, 0.5). The structure of the high-pressure phase is CsCl-type (B2-phase) (sc lattice with space group, Pm3m, No. 221) with positions of TM: (0, 0, 0) and N: (0.5, 0.5, 0.5). As mention earlier work [18, 20, 25], the TB-LMTO method works well for the close-packed structure and since the TMN compounds belongs to NaCl-type (B1-phase) structure at ambient conditions, which is not a close-packed one. We have therefore introduced two equivalent empty spheres at position (0.25, 0.25, 0.25) and (0.75, 0.75, 0.75) in such a way that they do not break the crystal symmetry [26]. However, the CsCl-type structure (B_2 -phase) is a closed-packed structure, and no such empty spheres were needed. The Wigner-Seitz sphere was chosen in such a way that the sphere boundary potential is minimum and the charge flow between the atoms is in accordance with the electro negativity criteria [20, 25]. The E and k convergences are checked subsequently to achieve better accuracy. The calculations were performed for 512 k points (grid of $8 \times 8 \times 8$) in the Brillouin zone for both the B_1 and B_2 phases.

The tetrahedron method [27] of Brillouin zone integration has been used to calculate the DOS. The total energy was computed by reducing the volume from $1.05V_0$ to $0.60V_0$, where V_0 is the equilibrium cell volume. The calculated total energy was fitted to Birch equation of states [28] to obtain the pressure volume relation. The pressure is obtained by taking the volume derivative of total energy. The Bulk modulus $B_T(-V_0 dP/dV_0)$ is also calculated from the P - V relations. The stability of a particular structure is decided by the minima of the enthalpy. The phase-transition pressure P_t can be obtained by matching enthalpies of both structure such that the difference of enthalpy $\Delta H(= H_{B_2} - H_{B_1})$ becomes zero at transition pressure (P_t).

3 Results and discussion

3.1 Structural properties

The electronic BS calculations are performed to estimate the total energy of TMN compounds by using the first principle TB-LMTO method. The total energies for the TiN and NbN compounds are plotted against different compressions and are shown in Figure 1(a)-(b). The minimum of all the curves define the equilibrium volume V_0 (or equilibrium separation a_0), which is found to be 17.23 \AA^3 and the corresponding lattice parameter is 4.1 \AA , which is underestimated by 3 % for TiN as compared to the experimental data [29]. Similarly, for NbN the estimated equilibrium volume is 7.44 \AA^3 with the corresponding lattice parameter as 3.1 \AA , which is underestimated by 0.2% as compared to the experimental data [6], which is listed in Table 1.

The present values of lattice parameters are in good agreement with the experimental values [29, 6]. However, experimentally [29, 6] reported values of the lattice parameters of TiN and NbN are little larger than our results. This is primarily due to usage of LDA [23] in the present calculation. Regarding the LDA contraction, it is often found that the LDA leads to some over binding which yields lattice parameters that are somewhat smaller when compared with the experimental.

Solids		$a_0 = 2r$ (Å)		B_T (GPa)		$N(E_f)$ (states/Ry cell)	P_t (GPa)	(V/V_0) %
		B_1	B_2	B_1	B_2			
TiN	Pres.	4.1	2.5	320	298	10.88	301.7	2
	Expt.	4.24 ^a	--	282 ^c	--	--	--	--
	Th.	4.246 ^b	2.63 ^h	277.9 ^h	253.8 ^h	--	364.1 ^h	--
NbN	Pres.	3.1	1.95	300	278	18.45	291	3
	Expt.	3.107 ^d	--	320 ^d	--	--	--	--
	Th.	3.114 ^e	2.721 ^e	349.5 ^e	332.7 ^e	--	290 ^e	--

^aRef[18], ^bRef[16], ^cRef[19], ^dRef[6], ^eRef[17].

Table 1. Calculated equilibrium lattice parameter a_0 (Å), bulk modulus B_T (GPa), number of f -states at the Fermi level $N(E_f)$ (states/Ry cell), phase transition pressure P_t in (GPa) of TM Nitrides in the B_1 and B_2 phases.

The calculation of transition pressure is carried out by estimating enthalpy in both the structures, as mentioned in Section 2. We have, therefore, plotted the variation of enthalpy with pressure for TiN and NbN in the B_1 and B_2 phases, shown as inset of Figure 1(a)-(b).

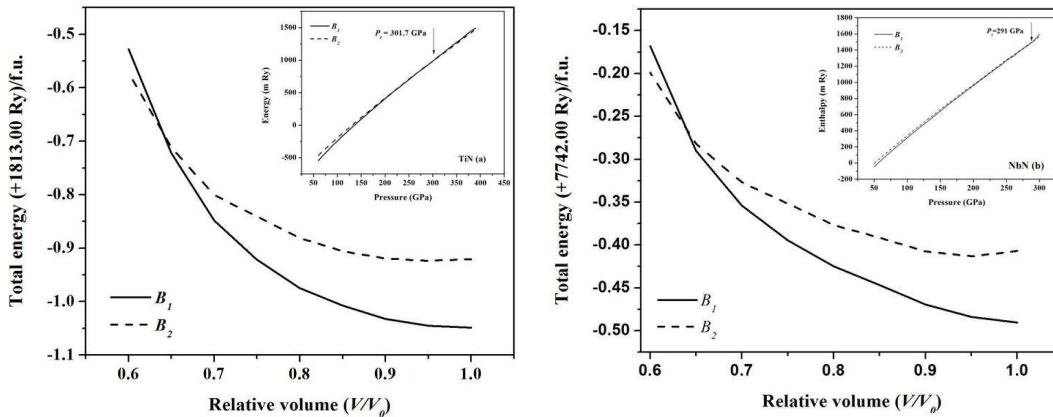


Figure 1. (a)-(b) Variation of total energy with relative volume for the B_1 and B_2 phase for TiN and NbN respectively. The inset shows the variation of enthalpies in the B_1 and B_2 phases for TiN and NbN.

The pressure at which these two phases coexist is phase-transition pressure. The equation of state in terms of pressure variation of relative volume change is given in Figure 2(a)-(b) for these TMN. In the case of TiN, we have predicted a phase transition pressure of 301.7 GPa with relative volume collapse of 2%. Similar phase transitions in NbN from the present calculations are also predicted, at pressure 291 GPa with relative volume collapse of 3%. The calculated values of phase transition pressure for both TMN are compared with theoretical results reported so far [16, 17]. The calculated bulk modulus values for TiN and NbN agree well with experimental and other theoretical values [6, 16, 17, 30].

3.2 Electronic properties

The electronic BS and the DOS for the TMN in their B_1 -phase under ambient conditions are shown in Figure 3(a)-(b). From these figures, it can be noticed that these compounds show metallic property which is manifested

by the presence of large number of *d*- and *f*-states at the Fermi level for TiN and NbN respectively, as mentioned in Table 1. To understand the elementary contribution of all atoms, we have studied the partial density of states (PDOS) which are shown in Figure 4.

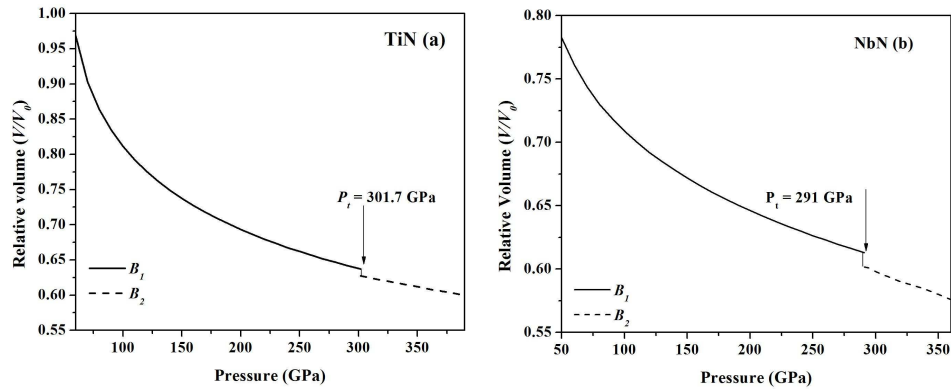


Figure 2. (a)-(b) Equation of states for TiN and NbN compounds. Solid line represents the B_1 phase and dotted line represents the B_2 phase.

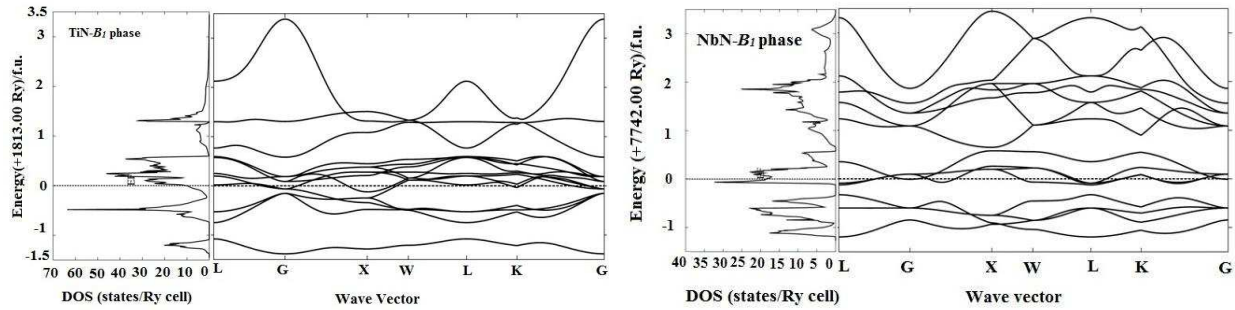


Figure 3. (a)-(b) BS and DOS in the B_1 phase for TiN and NbN respectively.

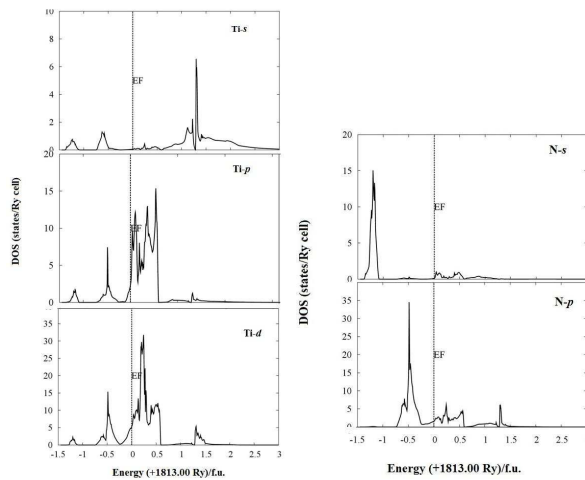


Figure 4. (a) PDOS in the B_1 phase for TiN.

From the PDOS analysis, it has been found that the lower valence band lying around -1.25 Ry is due to the N-*s* states for TiN and NbN. The upper valence band lying between -1.0 and 0.0 Ry are due to hybridization of Ti-*p*, *d*- and N-*p* states for TiN and Nb-*s*, *p*- and N-*p* states for NbN. The Ti-*d* and Nb-*f* states are highly localized at the Fermi level. The conduction bands are due to the hybridization of the Ti-*p* and Ti-*d* states at the Fermi level for TiN and Nb-*d* and Nb-*f* states for NbN.

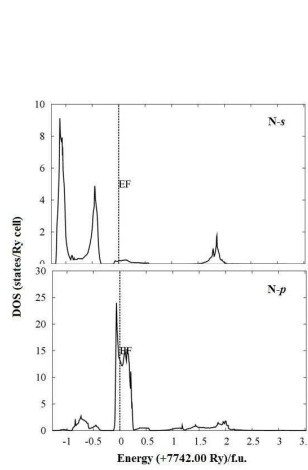


Figure 4. (b) PDOS in the B_1 phase for NbN.

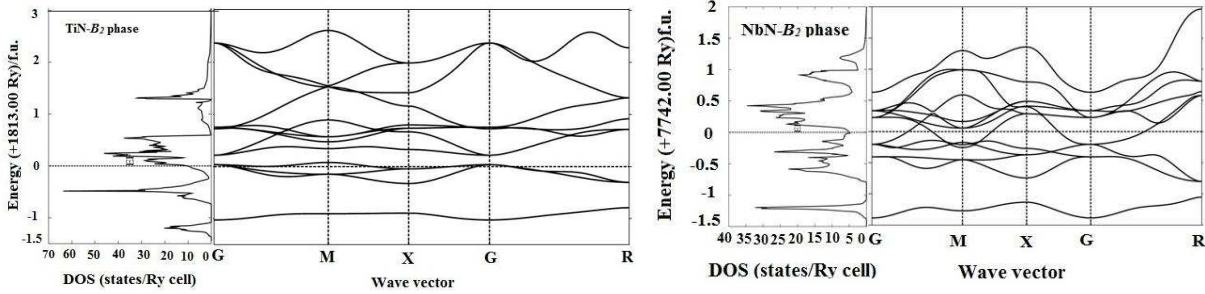


Figure 5. (a)-(b) BS and DOS in the phase for TiN and NbN respectively.

As pointed out earlier, the TMN compounds undergo structural phase transition from the B_1 to B_2 phases at the pressure of 301.7 and 291 GPa. Thus, the electronic BS and DOS for both compounds in the B_2 -phase are shown in Figure 5(a)-(b). The TMN retain their metallic property at high pressure also. The nature of the bands and DOS in the B_2 -phase is similar to the B_1 -phase for both the compounds, with a minor difference that the lower energy bands are shifted to the higher energy bands near the Fermi level and more compressed bands are seen for TiN and some upper bands are shifted to lower energy bands for NbN. The hybridization of the TM-*d*, -*f* and N-*p* states in the conduction band increases due to increase in pressure.

4 Conclusions

In summary, we have investigated structural and electronic properties for transition metal nitride using the TB-LMTO method within the LDA. At ambient conditions, these compounds are stable in the NaCl-type

structure and undergo structural phase transition to the CsCl-type structure in the pressure range 290-302 GPa. The lattice parameters, bulk modulus and the phase transition pressure are obtained which are in good agreement with the experimental data. The electronic properties of TiN and NbN under pressure are also calculated, and it is found that TiN and NbN exhibit a metallic behavior and the hybridizations between atoms become stronger under pressure.

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